WASHINGTON STATE
DEPARTMENT OF
ECOLOGY

Chemical Testing Methods for Designating Dangerous Waste

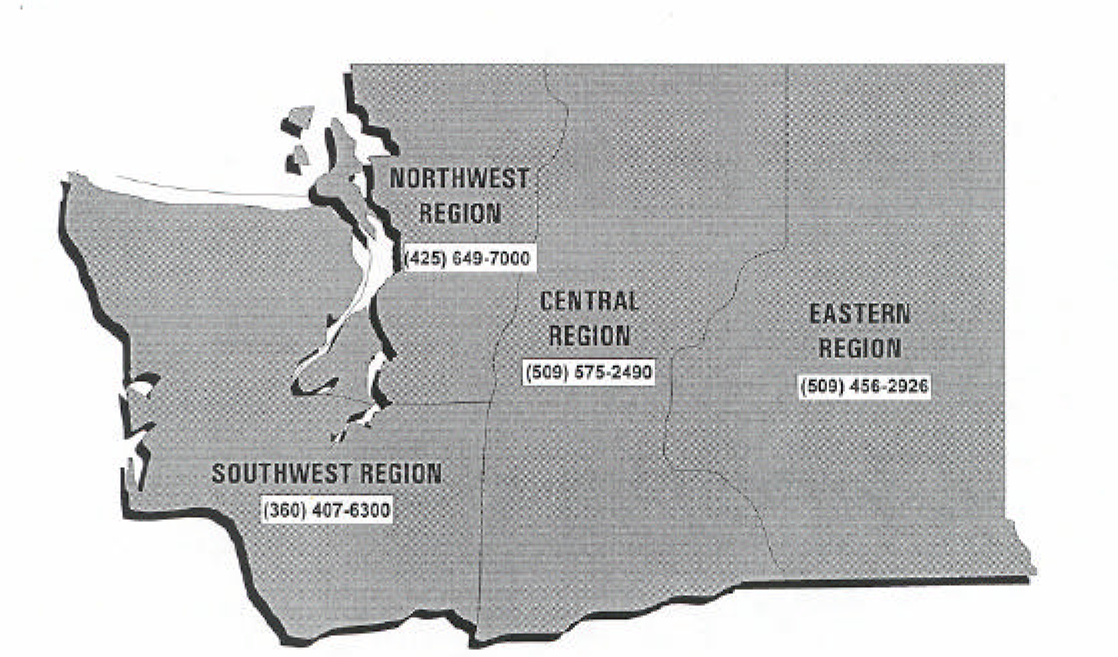
WAC 173 -3 03 -090 & 100

February 1998
Publication #97-407

For a copy of this document, please contact:

Department of Ecology
Publications
P.O. Box 47600
Olympia, WA 98504-7600

Please include your street address for UPS delivery



The Department of Ecology is an equal opportunity agency and does not discriminate on the basis of race, creed, color, disability, age, religion, national origin, sex, marital status, disabled veteran's status, Vietnam Era veteran's status or sexual orientation.

If you have special accommodation needs or require this document in alternative format, please contact the Hazardous Waste Reduction Program at (360) 407-6700 (Voice) or (360) 407-6006 (TDD).

Ecology's telecommunications device for the deaf (TDD) number is (360) 407-6006. Regional TDD numbers are:

CRO (TDD) (509) 454-7673
ERO (TDD) (509) 458-2055
NWRO (TDD) (425) 649-4259
SWRO (TDD) (360) 407-6306

Chemical Testing Methods for Designating Dangerous Waste

WAC 173 -3 03 -090 & 100

Hazardous Waste and Toxics Reduction Program
Olympia, WA 98504-7600

February, 1998

Prepared by Michelle Elling. For more information, please contact Ms. Elling at (360) 407-6704. Regional contacts are: Dennis Bowhay (CRO), Robert Carrell (Manchester Lab), Jim Knudson (HQ), Wayne Krafft (ERO), Viki Leuba (ERO), Vern Meinz (SWRO), Steve Robb (HQ), Stacie Singleton (HQ), Alex Stone (Kennewick), Bob Stone (NWRO), and Jerry Yokel (Kennewick).

This document is intended solely as guidance. No statutory or regulatory requirements are in any way altered by any statement(s) contained herein.

Table of Contents

TABLE OF CONTENTS, CONT.

Chapter 1

Introduction to Regulatory Testing Requirements

A. Introduction

This manual is intended to provide guidance for choosing chemical methods appropriate for the chemical testing of suspected dangerous wastes. In the State of Washington, the Dangerous Waste Regulations, Chapter 173-303 WAC, require all generators to designate their waste for the purposes of the rule, and to ensure proper management of the waste. "Dangerous wastes" means those solid wastes designated in WAC 173-303-070 through 173-303-100 as dangerous, or extremely hazardous or mixed waste.[1] Generators may either designate their waste based on process knowledge or by test methods accepted by the Department of Ecology (Ecology). Process knowledge may result, in part, from information such as Material Safety Data Sheets (MSDS).

Certain recycling activities, such as burning used oil for energy recovery, and dangerous waste management activities, such as land disposal, have specific regulatory testing requirements. For example, under the Land Disposal Restrictions (LDR) program, a restricted waste identified in the federal regulations with a corresponding concentration based treatment standard can be land disposed only if thresholds are not exceeded .[2] Table 1-1 identifies specific sections of the regulations that have testing requirements.

TABLE 1-1: Sections of the Rule That Have Regulatory Testing Requirements

WAC 173-303 Section	Section Title
173-303-090	Dangerous waste characteristics
173-303-100	Dangerous waste criteria
173-303-120	Recycled, reclaimed, and recovered wastes
173-303-140	Land disposal restrictions
173-303-300	General waste analysis
173-303-500	Recycling requirements for state-only dangerous waste
173-303-515	Special requirements for used oil burned for energy recovery

[1]As used in this manual, the words "dangerous waste" will refer to the full universe of wastes regulated by Chapter 173-303 WAC. The abbreviation "DW" will refer only to that part of the regulated universe which is not extremely hazardous waste.
[2]See 40 CFR 268.40.

A.1 Purpose

For the purpose of this guidance, Ecology is addressing the testing requirements of only two sections of the Dangerous Waste Regulations that have chemical testing requirements. Those sections are WAC 173-303-090, Dangerous Waste Characteristics, and WAC 173-303-100, Dangerous Waste Criteria. This is not meant to imply that generators have satisfied regulatory testing requirements by following the test methods specified in this document. **If a waste is managed in such a way that regulatory requirements other than WAC 173-303-090 and -100 apply to that waste stream, a generator must also comply with the testing requirements of those other sections.**

A.2 Dangerous Waste Characteristics and Criteria

Dangerous waste characteristics are defined under the following four categories: ignitability; corrosivity, reactivity, and the toxicity characteristic. Chapter 2 of this guidance is dedicated to the four characteristics which are based in large part on federal requirements.

Dangerous waste criteria are defined as toxic dangerous wastes and persistent dangerous wastes. The State of Washington developed these criteria in addition to the federal characteristics. The acute toxicity of a waste is determined by the methods in Biological *Testing Methods*, WDOE 80-12 (most recent revision), or may be determined by book designation[3] when knowledge of the waste is sufficient. Toxicity criteria and book designation are addressed in Chapter 3. Persistent dangerous wastes are defined as chemical compounds which are either halogenated organic compounds (HOC), or polycyclic aromatic hydrocarbons (PAH). Persistent dangerous waste definitions and appropriate test methods are identified in Chapter 3 of this guidance.

For each characteristic and criteria that is addressed in this guidance, you will find: (1) a narrative description of the characteristic or criteria, (2) the regulatory description of the characteristic or criteria, and (3) in Appendix 3, a test method giving details for the laboratory analyst conducting such tests.

[3] Book designation is possible when a generator has sufficient knowledge of the process that created the waste to identify the constituents of concern in that waste stream. In this instance, a generator might use an MSDS to identify a reactive waste. Commonly, book designation is used in determining toxic wastes using such references as The National Institute for Occupational Safety and Health's (NIOSH) Registry of Toxic Effects of Chemical Substances (RTECS).

Chapter One

B. Methods for Designating Dangerous Waste

Not all test methods accepted by Ecology are included in this guidance. Some of the included test methods reference other methods because of copyright restrictions (e.g., ASTM) or length (e.g., EPA analytical methods). Therefore, to promote standardization and consistency, this guidance references the EPA publication *Test Methods for Evaluating Solid Waste -Physical/Chemical Methods, SW-846,* the most recent revision.

Certain methods are mandated specifically in the regulations, such as methods for characteristic wastes and in determining free liquid for LDR regulations. When methods are not specified by the rules, any reliable method may be used for hazardous waste testing. In these cases, the analytical method chosen by the generator must provide enough information to make the regulatory decision. The test must be able to identify the analytes of concern, at the regulatory level of concern, in the matrix of concern, with sufficient accuracy and precision.

Because a waste can be liquid, solid, or gaseous, there are several standardized methods available other than *SW-846.* At this time, Ecology recognizes methods from the following sources:

1. *Test Methods for Evaluating Solid Waste, SW-846,* EPA;
2. *Standard Methods for the Examination of Water and Wastewater*, most current edition;
3. *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*, EPA *600/4-79-020,* EPA;
4. National Association of Corrosion Engineers;
5. The American Society for Testing and Materials (ASTM); and
6. Air Pollution Training Institute (APTI), National Technical Information Service.

These methods are available so that a generator can choose a method that is matrix specific and precise enough to provide the information necessary for a regulatory decision. Therefore, it is important that the generator of the waste consult with their analytical laboratory on which analysis will meet their regulatory needs. Ecology strongly recommends the use of laboratories that are accredited, as this is an indicator of the quality of a lab's work.'

[4] Washington State's accreditation program for laboratories currently accredits for water methods, only (Chapter 173-050 WAC). A list of accredited labs is available on the Internet at http://www.wa.gov/ecology or can be obtained from any of Ecology's regional offices. For more information about Ecology's laboratory accreditation program, refer to publication #91-34, *Procedural Manual for the Environmental Laboratory Accreditation Program,* January 1994.

Chapter 2

Dangerous Waste Characteristics: WAC 173-303-090

A. Ignitability

A.l Introduction

The objective of the ignitability characteristic is to identify wastes that either present fire hazards during routine storage, disposal, and transportation or, once started, are capable of severely exacerbating a fire. Most ignitable wastes are liquids. Solids, ignitable compressed gases, and oxidizers may also create ignitability hazards.

Liquids and solids do not typically burn. They give off vapors that ignite only when a combustible mixture with air or another oxidizer has been attained. Some ignitable liquids give off insufficient vapor to burn at their ambient temperatures. The liquid must be heated to a temperature at which the concentration of the vapor is within its flammable range before it can ignite. The concentrated vapor will usually beat or just above the surface of the liquid or solid.

A.l.a Definition of Flash Point

The United States Department of Transportation (USDOT)[5] defines the flash point as 'the minimum temperature at which a substance gives off flammable vapors which, in contact with sparks or flame, will ignite.' In other words, the flash point is the minimum temperature at which a liquid gives off sufficient vapor to first form an ignitable mixture with the air near the surface of the liquid or within a test vessel. A substance does not continuously burn at its flash point; the ignitable mixture only momentarily flashes. Flash points are determined in specialized scientific apparatus, such as those specified in Appendix 3.13, Analyses for the Ignitability Characteristic.

A.l.b Methods for Determining Flash Point

The methods specified in Appendix 3.13 use a closed cup tester to measure flash point. The closed cup analyses for **flash point are not appropriate for solids, but for liquids only.** While flash point is used only for liquids, no specific definition of the term "liquid" exists with respect to this characteristic in the regulations. Method 9095A, the

[5] 49 CFR § 173.120

paint filter liquids test, has been the traditional method of determining whether a waste contains liquids for land disposal regulations (LDR). This analysis would ban a waste from land disposal if one drop of liquid was produced through the filter. Therefore, sludge might be required to be tested for ignitability.

To clarify this issue, EPA produced guidance on procedures for determining if a waste contains a liquid on January 13, 1995.[6] "The **definitive procedure** for determining if a waste contains a liquid for the purposes of the ignitability and corrosivity characteristics is the **pressure filtration technique specified in Method 1311.** However, if one obtains a free liquid phase using Method 9095A, a free liquid phase using Method 9095A should then be assessed for the presence of an ignitable or corrosive liquid using the pressure filtration technique specified in Method 1311."

For purposes of WAC 173-303-090(5)(a)(i), the test liquid is introduced to a standard closed container and an ignition source supplied. If the test liquid flashes (ignites), the waste meets the characteristic of ignitability. Waste liquids, such as gasoline, are designated as dangerous wastes if their flash point is less than 140 degrees F using the standard testing methods specified in the WAC 173-303-090(5)[7] and/or in Appendix 3.13.

When an aqueous[8] waste is composed of less than 24 percent alcohol and that waste is ignitable based on the alcohol content of the waste stream, a generator need not designate this waste as ignitable. This is commonly referred to as the "alcohol exclusion". The term "alcohol" refers to any alcohol or combination of alcohols. The alcohol exclusion is intended to exempt alcoholic beverages and some types of latex paints, which exhibit low flash points due to the alcohol content but do not sustain combustion because of the high water content.

While the concept of a substance's flash point is useful for describing the ignitability of liquids, the term does not ordinarily have meaning when applied to ignitable gases or solids. At ambient conditions, most ignitable gases do not need to be heated in order to ignite. Therefore, ignitable wastes, other than liquids, are identified through narrative regulatory definition and/or by the test methods described by the regulations.

A.l.c National Fire Protection Association (NFPA) Classification for Oxidizers

The characteristic of ignitability may also be applied to a waste that is an oxidizer. Oxidizing agents are relatively powerful chemical substances and they readily react with a large group of other substances. The degree of hazard of oxidizers may be evaluated by

[6] 60 CFR 3092
[7] ASTM Standard D-93-79, D-93-80, or D-3278-78.
[8] See Chapter 2, Section B.l.b for more information on how to determine if a waste is aqueous.

consideration of the National Fire Protection Association (NFPA) classification for oxidizers[9].

Class 1 oxidizer: An oxidizing material whose primary hazard is that it may increase the burning rate of combustible material with which it comes in contact.

Class 2 oxidizer: An oxidizing material that will moderately increase the burning rate or that may cause spontaneous ignition of combustible material with which it comes in contact.

Class 3 oxidizer: An oxidizing material that will cause a severe increase in the burning rate of combustible material with which it comes in contact or that will undergo vigorous self-sustained decomposition when catalyzed or exposed to heat.

Class 4 oxidizer: An oxidizing material that can undergo an explosive reaction when catalyzed or exposed to heat, shock, or friction.

Thus, the relative degree of hazard increases in the following order for oxidizers: 4 greater than 3 greater than 2 greater than 1. Table 2-1 illustrates examples of oxidizers in each NFPA class.[10]

A.2 Regulatory Definition; Ignitable Characteristic

The following definitions are from the Dangerous Waste Regulations (WAC 173-303-090). Department of Transportation (DOT) regulatory definitions associated with the ignitable characteristic can be found in Appendix 2.

A solid waste exhibits the characteristics of ignitability if a representative sample. of the waste has any of the properties listed below. A solid waste that exhibits the characteristic of ignitability must be designated DW and assigned the dangerous waste number of D001.

A.2.a Ignitable Liquids

An ignitable liquid is a liquid, other than an aqueous solution containing less than 24 percent alcohol by volume for which the liquid has a flash point less than 60 degrees C (140 degrees F) based on the alcohol content; which has a flash point less than 60 degrees Celsius (C) (140 degrees Fahrenheit (F)), as. determined by a Pensky-Martens Closed Cup

[9] NFPA 43A -1980, Code for the Storage of Liquid and Solid Oxidizing Materials.
[10] For those concentrations not otherwise specified in Table 2-1, the concentration levels is at 100 % .

TABLE 2-1: Some Typical Oxidizers by NFPA Classification

Class 1	
Aluminum nitrate	Potassium dichromate
Ammonium persulfate	Potassium nitrate
Barium chlorate	Potassium persulfate
Barium nitrate	Silver nitrate
Calcium chlorate	Sodium carbonate peroxide
Calcium nitrate	Sodium dichloro-s-triazinetrione dihydrate
Calcium peroxide	Sodium dichromate
Cupric nitrate	Sodium nitrate
Hydrogen peroxide solutions over 8 percent but not exceeding 27.5 percent concentration by mass	Sodium nitrite
Lead nitrate	Sodium perborate
Lithium hypochlorite	Sodium perborate tetrahydrate
Lithium peroxide	Sodium perchlorate monohydrate
Magnesium nitrate	Sodium persulfate
Magnesium perchlorate	Strontium chlorate
Magnesium peroxide	Strontium peroxide
Nickel nitrate	Thorium nitrate
Nitric acid solutions, 70 percent concentration or less	Uranium nitrate
Perchloric acid solutions, less than 60 percent by mass	Zinc chlorate
	Zinc peroxide
Class 2	
Calcium hypochlorite solutions, 50 percent or less by mass	Potassium permanganate
Chromium trioxide (chromic acid)	Sodium chlorite solutions, 40 percent or less
Halane (1,3-dichloro-5,5-dimethyl hydantoin)	Sodium peroxide
Hydrogen peroxide, 27.5 percent to 52 percent concentration by mass	Sodium permanganate
Nitric acid solutions, more than 70 percent concentration	Trichlor-s-triazinetrione (tricloroisocyanuric acid)
Class 3	
Ammonium dichromate	Potassium bromate
Calcium hypochlorite, over 50 percent by mass	Potassium chlorate
Hydrogen peroxide, 52 percent to not more than 91 percent concentration by mass	Potassium dichloro-s-triazinetrione (potassium dichloroisocyanurate)
Mono-(trichloro)tetra-(monopotassium dichloro)-penta-s-triazinetrione	Sodium chlorate
Perchloric acid solutions, 60 percent to 72.5 percent by mass	Sodium chlorite solutions , over 40 percent by mass
	Sodium dichloro-s-triazinetrione (sodium dichloroisocyanurate)
Class 4	
Ammonium perchlorate	Perchloric acid solutions, more than 72.5 percent by mass
Ammonium permanganate	Potassium superoxide
Guanidine nitrate	
Hydrogen peroxide solutions, more than 91 percent by mass	

Tester[11], as specified in ASTM Standard D-93-79 or D-93-80[12], or a Setaflash Closed Cup Tester[13], as specified in ASTM standard D-3278-78.

The DOT definition for ignitable liquids can be found in Appendix 2.A.

A.2.b Ignitable Solids

An ignitable solid waste that is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture, or spontaneous chemical changes and, when ignited, burns so vigorously and persistently that it creates a hazard.

The phrase "under standard temperature and pressure," means 20 degrees Celsius (68 degrees Fahrenheit) and 1 atmosphere. Examples of ignitable solids include metallic magnesium, metallic sodium, and white phosphorous.

A.2.c Ignitable Compressed Gases

An ignitable compressed gas is a compressed gas which is defined in US DOT Regulations at 49 CFR § 173.115 and is determined to be flammable by the test methods described in that regulation. Additional definitions for ignitable compressed gases can be found in Appendix 2.B, the DOT definition for ignitable compressed gases.

A.2.d Oxidizers

A waste is an oxidizer, if it is defined as such in 49 CFR § 173.127 and 49 CFR § 173.128. For the purpose of WAC 173-303-090(5)(a)(iv), an oxidizer is any material that yields oxygen readily to support the combustion of organic matter.

Additional definitions for oxidizers. and organic peroxides can be found in Appendix 2.C, the DOT definition for oxidizers.

[11]SW-846 Method 1010, found in Appendix 3.B.1.
[12]ASTM standards are available from ASTM, 1916 Race Street, Philadelphia, PA 19103.
[13] SW-846 Method 1020A, found in Appendix 3.B.2.

B. Corrosivity

B.l Introduction

Corrosion refers to a chemical process in which metals and minerals are converted into undesirable by-products. Corrosion is caused by any substance that spontaneously eats into or destroys either metals or minerals, such as acids and bases. Furthermore, corrosion is not limited to the action of such substances on metals and minerals alone. Corrosion also refers to the destructive action such substances have on certain metallic compounds, as well as on human, plant or animal tissue.

Possible hazards of wastes that exhibit the characteristic of corrosivity are:

1. Mobilization of toxic metals if discharged into a landfill environment; or

2. Corrosion of handling, storage, transportation, and management equipment; or

3. Destruction of human, animal, or plant tissue in the event of contact.

In order to identify such potentially hazardous materials, Chapter 173-303 WAC has identified two properties upon which to base the definition of a corrosive waste. These properties are pH and corrosivity toward Type SAE 1020 steel.

B.1.a Definition of pH

The pH is a measure of the acidity and/or alkalinity of a solution. Aqueous solutions having a pH of 7 are neutral. The value increases with greater alkalinity and decreases with greater acidity. Mathematically, pH is the negative logarithm of the hydrogen ion concentration in water.

B.l.b Methods for Determining pH

A common method of indicating pH is through the use of pH testing papers. An approximate pH of a waste can be determined with wide-range pH paper. Litmus is probably the most common wide range pH paper used to differentiate acids from bases. Derived from certain lichens, a solution of litmus is allowed to impregnate strips of paper, which are then dried. When moistened with an aqueous acid, litmus paper turns red; when moistened with a basic solution, it turns blue. More accurate pH determinations can be made using "narrow-range" pH paper whose accuracy has been determined (1) using a series of buffers or (2) by comparison with a calibrated pH meter.

Although narrow-range pH paper can be purchased with a distinct color change for every 0.5 pH unit, pH paper is not considered to be as accurate a form of pH measurement as pH meters. For this reason, pH measurements taken with pH paper cannot be used to definitively designate a waste as corrosive or noncorrosive for the purposes of regulation. In a chemical laboratory, the pH is frequently determined by means of an electrometric measurement using an apparatus called a pH meter. A pH meter is a voltage-measuring device attached to a pair of electrodes. When the tips of the electrodes have been immersed in a solution, the pH of the solution can readily be established simply by reading the scale. The scale is established when the pH meter is calibrated using predetermined standards. Wastes with greater than 20 percent aqueous content should be tested using SW-846 Method 90408[14]. Wastes with less than 20 percent aqueous content are considered solid or semi-solid wastes, and should be analyzed using SW-846 Method 9045C.

SW-846 Method 9045C[15] is the analysis for solid or semi-solid wastes for corrosivity[16]. In this analysis, wastes with 20 percent or less aqueous content are mixed with an equal weight of water. The liquid portion of this newly generated suspension or solution will be tested using a pH meter, after the solid portion of the waste has settled. It is important to note that for solid or semi-solid waste, that the liquid portion of the waste is not decanted off and analyzed for pH.

B.2 Regulatory Definition; Corrosive Characteristic

A solid waste exhibits the characteristic of corrosivity if a representative sample of the waste has any of the following properties:

a. It is aqueous and has a pH less than or equal to 2, or greater than or equal to 12.5, as determined by a pH meter using Method 90408 in *Test Methods for Evaluating Solid Waste Physical/Chemical Methods*, EPA publication SW 846, as incorporated by reference in WAC 173-303-110 (3)(a); or

b. It is a liquid and corrodes steel (SAE 1020) at rate greater than 0.250 inch (6.35 mm) per year at a test temperature of 55 degrees C (130 degrees F), as determined by the test method specified in NACE (National Association of Corrosion Engineers) Standard TM-O1-69, as standardized

[14] SW-846 Method 90408, found in Appendix 3.C.1. Aqueous content is based on testing limitations. SW-846 defines a liquid as having greater than 20 percent aqueous content. A solid has less than 20 percent aqueous content.
[15] SW-846 Method 904513, found in Appendix 3.C.2.
[16] WAC 173-303-090(6)(a)(iii).

in *Test Methods for Evaluating Solid Waste Physical/Chemical Methods*[17]", EPA publication SW 846, as incorporated by reference in WAC 173-303-110 (3)(a); or

c. It is solid or semi-solid which, upon testing using Method 9045C in *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW* 846), results in a pH less than or equal to 2, or greater than or equal to - 12.5.

A solid waste that exhibits the characteristic of corrosivity because:

1. It has either of the properties described in 'a' or 'b', above, will be designated DW, and assigned the dangerous waste number of D002;

2. It only has the property described in 'c', above, will be designated DW, and assigned the dangerous waste number of WSC2.

C. Reactivity

C.1 Introduction

Reactive wastes include wastes that have any of the following properties:

1. Readily undergo violent chemical change;
2. React violently or form potentially explosive mixtures with water;
3. When mixed with water generate toxic fumes or, in the case of cyanide- or sulfide-bearing wastes, generate toxic fumes when exposed to mildly acidic or basic conditions;
4. Explode when subjected to a strong initiating force;
5. Explode at normal temperatures and pressures; or
6. Fit within the Department of Transportation's forbidden explosives, Class 1 explosive; Division 1.1, Division 1.2, Division 1.3, and Division 1.5 explosives classifications.

These properties were chosen to identify wastes that, because of their extreme instability and tendency to react violently or explode, pose a threat to human health and the environment at all stages of the waste management process.

[17] SW-846 Method 1110, found in Appendix 3,C.3.

C.1.a Water Reactive Wastes

Water may react or interact with hazardous materials in a number of potentially dangerous ways. Water may react with a substance to form a product that is either flammable, explosive, toxic, or corrosive. The process whereby water causes the decomposition of a substance is called hydrolysis. Not all hydrolysis reactions result in the formation of products that have potentially dangerous properties.

Water may cause or aggravate a potentially hazardous situation in other ways. For instance, some substances absorb atmospheric water vapor, and are said to be hygroscopic. Two examples of hygroscopic substances are sodium hydroxide and concentrated sulfuric acid. A full container of concentrated sulfuric acid will overflow its container when left to stand in humid air.

C.1.b Chemical Explosive Wastes

A chemical explosive is a substance that detonates spontaneously or as the result of friction, mechanical impact, or heat. It is ordinarily perceived as a substance whose primary intended purpose is to accomplish some act, like demolition, when it detonates. In this latter regard, chemical explosives are distinguished from certain other substances, like gasoline or flammable gases, which when confined in containers and ignited may explode. They are also distinguished from nuclear explosives, which detonate certain nuclear phenomena.

C.2 Regulatory Definition; Reactive Characteristic

A solid waste exhibits the characteristic of reactivity if a representative sample of the waste has any of the following properties:

1. It is normally unstable and readily undergoes violent change without detonating;

2. It reacts violently with water;

3. It forms potentially explosive mixtures with water;

4. When mixed with water, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment;

5. It is a cyanide- or sulfide-bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a

danger to human health or the environment.[18] The current EPA guidance level for total releasable cyanide is 250 mg HCN/kg waste. The current EPA guidance level for total releasable sulfide is 500 mg H_2S/kg waste;

6. It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement;

7. It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure;[19] and

8. It is a forbidden explosive, as defined in 49 CFR § 173.54, or a Class 1 explosive, Division 1.1, Division 1.2, Division 1.3, and Division 1.5, as defined in 49 CFR § 173.50.

A solid waste that exhibits the characteristic of reactivity must be designated DW, and assigned the dangerous waste number of D003.

D. Toxicity Characteristic

D.1 Introduction

The study of adverse health effects caused by poisonous or toxic substances is called toxicology. Poisons or toxins are generally regarded as those substances that cause or contribute to illness or death when administered to an organism in good health in relatively small amounts. The basic principles of toxicology comprise an important segment of the study of hazardous materials.

In the state of Washington, toxic wastes are addressed in two ways; under the toxicity characteristic as determined by the Toxicity Characteristic Leaching Procedure (TCLP) or as a toxic dangerous waste under the dangerous waste criteria.[20]

D.1.a Toxicity Characteristic Leaching Procedure (TCLP)

The origins of the TCLP and its precurser, , Extraction Procedure (EP) Toxicity Test, rest in the model of the leaching a waste will undergo if disposed of in a landfill containing municipal solid waste. The decomposing municipal solid waste produces a slightly acidic leachate (pH 5.0) that extracts hazardous constituents from the waste and then migrates to

[18] Interim Guidance for Reactive Cyanide and Reactive Sulfide, Steps 7.3.3 and 7.3.4 in Appendix 3.D, can be used to detect the presence of reactive cyanide and reactive sulfide in wastes.
[19] With standard temperature being 20 degrees Celsius and standard pressure being 760 mm of Hg (1 atm).
[20] WAC 173-303-100(5)

ground water. Once in the ground water, the contaminants migrate to an underground source of drinking water.

In order to establish the concentration limits for the toxicity characteristic, EPA's model assumed that the landfill leachate would be diluted or otherwise attenuated by a factor of 100 before reaching a drinking water source. Therefore, toxicity characteristic (TC) concentration levels were established at 100 times drinking water standards or other health based standards. This is commonly referred to as the dilution attenuation factor, or DAR

For TCLP, a subsample of a waste is extracted with the appropriate buffered acetic acid solution for approximately 18 hours. The extract obtained from the TCLP (the "TCLP extract") is then analyzed to determine if any of the thresholds established for the 40 TC constituents have been exceeded.[21] Table 2-2 lists the regulatory thresholds for the TC constituents and SW-846 methods used for analyzing the TCLP extract. This list of methods is not all inclusive, as other methods may be equally reliable and approved by the department for use in designating toxic wastes.

D.1.b Methods for Determining Toxicity

In the early history of RCRA and the DW Regulatory program EP Toxicity Test, SW-846 Method 1310, was promulgated for characteristic identification in determining the toxicity of fourteen substances. In 1990, the TCLP procedure was established. SW-846 Method 1311 evaluates the leachability of the same fourteen substances included in Method 1310, but adds an additional twenty-six organic compounds to be determined. The procedure is set out in full in Appendix 3.E. The TCLP consists of five steps (refer to Figure 3):

D.1.b.ISeparatioh Procedure

For liquid waste (i.e., for the purpose of the TCLP, those containing less than 0.5 percent dry solid material), the waste (liquid portion), after filtration through a 0.6 to 0.8 gm glass fiber filter, is defined as the TCLP extract.

For wastes containing greater than or equal to 0.5 percent solids, the liquid, if any, is separated from the solid phase and stored for later analysis:

D.L&2Particle Size Reduction

[21] WAC 173-303-090(8)(c); 40 CFR §261.24

Prior to extraction, the solid material must pass through a 9.5-mm (0.375-in.) standard sieve, have a surface area per gram of material equal to or greater than 3.1 cm^2, or, be smaller than 1 cm in its narrowest dimension. If the surface area is smaller or the particle size larger than described above, the solid portion of the waste is prepared for extraction by crushing, cutting, or grinding the waste to the surface area or particle size described above. (Special precautions must be taken if the solids are prepared for organic volatiles extraction.)

D. I.b.3Extractiou of Solid Material

The solid material from D.l.b.2 is extracted for approximately 18 hours with an amount of extraction fluid equal to 20 times the weight of the solid phase[22]. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes.

D.Lb.4Fiual Separation of the Extraction from the Remaining Solid

Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 ~tm glass fiber filter. If compatible, the initial liquid phase of the waste (from D.l.b.l) is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

D. 1. b.5 Testing (Analysis) of TCLP Extract

Inorganic and organic species are identified and quantified using appropriate methods in the 6000, 7000, and 8000 series of SW-846 methods in this manual or by equivalent methods.[23]

D.2 Regulatory Definition; Toxicity Characteristic

A solid waste exhibits the characteristic of toxicity if, using the *Toxicity Characteristic Leaching Procedure (TCLP* found in Appendix 3.E) test method 1311 in *Test Methods for Evaluating Solid Waste Physical/Chemical Methods* (SW 846), the extract from a representative sample of

[22] Refer to D.1.b.1 for the liquid portion of a waste containing greater than or equal to 0.5 percent solids.
[23] Equivalent testing methods as described in WAC 173-303-110(5).

the waste contains any of the contaminants listed in the toxicity characteristic list in Table 2-2, at concentrations equal to or greater than the respective value given in the list. When the waste contains less than 0.5 percent filterable solids, the waste itself, after filtering using the methodology outlined in Method 1311, is considered to be the extract for the purpose of this subsection.

A solid waste that exhibits the toxicity characteristic has the dangerous waste number specified in Table 2-2 which corresponds to the toxic contaminant causing it to be dangerous. Any waste that contains contaminants which occur at concentrations at or above the regulatory threshold must be designated DW.

TABLE 2-2 Maximum Concentration of Contaminants for the Toxicity Characteristic

Dangerous Waste Number	Contaminant	(Chemical Abstracts Services #)	Regulatory Level DW (mg/L)	SW 846 Test Methods after 1311
D004	Arsenic	(7440-38-2)	5.0	6000 or 7000 series
D005	Barium	(7440-39-3)	100.0	6000 or 7000 series
D018	Benzene	(71-43-2)	0.5	8021B, 8260B
D006	Cadmium	(7440-43-9)	1.0	6000 or 7000 series
D019	Carbon tetrachloride	(56-23-5)	0.5	8021B, 8260B
D020	Chlordane	(57-74-9)	0.03	8081A
D021	Chlorobenzene	(108-90-7)	100.0	8021B, 8260B
D022	Chloroform	(67-66-3)	6.0	8021B, 8260B
D007	Chromium	(7440-47-3)	5.0	6000 or 7000 series
D023	o-Cresol	(95-48-7)	200.0[1]	8270C
D024	m-Cresol	(108-39-4)	200.0[1]	8270C
D025	p-Cresol	(106-44-5)	200.0[1]	8270C
D026	Cresol		200.0[1]	8270C
D016	2,4-D	(94-75-7)	10.0	8151A
D027	1,4-Dichlorobenzene	(106-46-7)	7.5	8021B, 8260B
D028	1,2-Dichloroethane	(107-06-2)	0.5	8021B, 8260B
D029	1-1-Dichloroethylene	(75-35-4)	0.7	8021B, 8260B
D030	2,4-Dinitrotoluene	(121-14-2)	0.13	8270C
D012	Endrin	(72-20-8)	0.02	8081A

TABLE 2-2 Maximum Concentration of Contaminants for the Toxicity Characteristic, Cont.

Dangerous Waste Number	Contaminant	(Chemical Abstracts Services #)	Regulatory Level DW (mg/L)	SW 846 Test Methods
D031	Heptachlor (and its epoxide)	(76-44-8)	0.008	8081A
D032	Hexachlorobenzene	(118-74-1)	0.13	8081A, 8121, 8270C
D033	Hexachloro-1,3-butadiene	(87-68-3)	0.5	802113, 826013
D034	Hexachloroethane	(67-72-1)	3.0	8270C
D008	Lead	(7439-92-1)	5.0	6000 or 7000 series
D013	Lindane	(58-89-9)	0.4	8081A
D009	Mercury	(7439-97-6)	0.2	6000 or 7000 series
D014	Methoxychlor	(72-43-5)	10.0	8270C, 8081A
D035	Methyl ethyl ketone	(78-93-3)	200.0	8260B
D036	Nitrobenzene	(98-95-3)	2.0	8270C
D037	Pentachlorophenol	(87-86-5)	100.0	8270C
D038	Pyridine	(110-86-1)	5.0	8270C
DO10	Selenium	(7782-49-2)	1.0	6000 or 7000 series
13011	Silver	(7440-22-4)	5.0	6000 or 7000 series
D039	Tetrachloroethylene	(127-18-4)	0.7	802113, 826013
D015	Toxaphene	(8001-35-2)	0.5	8081A
D040	Trichloroethylene	(79-01-6)	0.5	802113, 8260B
D041	2,4,5-Trichlorophenol	(95-95-4)	400.0	8270C
D042	2,4,6-Trichlorophenol	(88-06-2)	2.0	8270C
D017	2,4,5-TP (Silvex)	(93-72-1)	1.0	8151A
D043	Vinyl chloride	(75-01-4)	0.2	802113, 826013

[1] If o-, m-, and p-cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level of total cresol is 200 mg/L.

Chapter 3

Dangerous Waste Criteria: WAC 173-303-100

A. Introduction to State Criteria Wastes

The federal environmental program administered by the Environmental Protection Agency (EPA) regulates what is called hazardous waste (HW). EPA designates wastes as hazardous by: either a `listed' waste (F, K, P, U); or a waste that fails the characteristic tests of ignitability, corrosivity, reactivity, and/or toxicity.

Washington State's environmental program is administered by the Department of Ecology. Under Chapter 173-303 WAC, the Dangerous Waste regulations, waste can designate as dangerous waste (DW) or extremely hazardous waste (EHW). Ecology has generally incorporated EPA's lists and characteristics verbatim as the state's dangerous waste designation method. In addition, Ecology has chosen to designate wastes which fail certain criteria (fish / oral rat acute toxicity, and persistence). These are often referred to as "State-only" criteria to distinguish them from the federal lists and characteristics.

The state-only criteria depend on tests and/or knowledge about a waste and its constituents. Responsibility is placed on the generator to determine whether the waste passes or fails the criteria. EPA has no counterpart in its designation approach to these state-only criteria.[24]

Generators may need to determine if a solid waste meets the state-only criteria. If a waste stream designates as either a characteristic waste or a listed waste, the generator, generally, needs not determine whether the waste fails the state-only criteria. The three circumstances described in WAC 173-303-070(5) covers those instances when a generator would need to do additional designation of waste already determined to be DW. First, when a generator qualifies as a small quantity generator, the generator must determine if their DW is also designated as toxic EHW. Second, when a generator is discharging their DW waste to a Publicly Owned Treatment Works (POTW) operating under a permit-by-rule in accordance with WAC 173-303-802(5), the generator must determine if the waste is also an EHW. Third, if the waste is designated as a state-only DW, the generator must also perform additional designation if the waste will be burned for energy recovery as used oil under WAC 173-303-515 or if the waste will be land disposed within Washington State. When the state-only DW will be burned for energy recovery as used oil in accordance with WAC 173-303-515, additional designation is required to see if the state-only DW is also a toxic or persistent waste. When the state-only DW will be land disposed

[24]Although EPA does not have a regulatory counterpart for criteria wastes, EPA does use acute toxicity and persistence as the basis for listing a waste.

within the state, additional designation is required to see if the waste designates as an EHW25. The other exception to this rule is under the domestic sewage exclusion. Under this exclusion, ail the waste, prior to mixing with domestic sewage, must not meet the dangerous waste criteria for toxicity or persistence unless it is treatable by the receiving POTW.

A.1 Background for Toxic Criteria Wastes .

In 1978, when Ecology promulgated the first dangerous waste regulations, Ecology believed that regulating dangerous waste that exhibits the criteria of acute mammalian toxicity is necessary for safe management of dangerous waste, especially in storage, packaging, transporting, spill response, treatment, and disposal. Mammalian toxicity continues to be an important criteria to help prevent future problems with direct ingestion at abandoned disposal sites. For mammalian toxicity, Ecology borrowed accepted acute toxicity criteria and testing methods from the work done in the federal pesticide laws (Acute Oral Rat Toxicity Test).

To address acute toxicity to non-mammals, Ecology also included acute fish toxicity with the toxic criteria wastes. Acute fish toxicity reflects the biological impact from waste components that, for the most part, can be solubilized in the course of testing; i.e., in water. Other non-soluble portions of the waste, such as oils and particulate matter, can also significantly affect the outcome of the acute fish toxicity analysis. The fish used in this analysis will have fasted prior to the beginning of the test and tend to be surface feeders, therefore, floating material that has not solubolized may be consumed by the fish and affect the outcome of the analysis. In this way, the fish toxicity test can then `model' the disposal environment in such events as illegal dumping of waste into a stream or lake.

A framework for toxicity was developed for acute fish toxicity based on the work of the United Nations' Intergovernmental Maritime Consultative Organization (IMCO) system and EPA's hazardous material spill regulations promulgated under Section 311 of P.L. 92-500.

A.2 Background for Persistent Criteria Wastes

Initially, one of the major challenges Ecology encountered with the dangerous waste designation system was the legislative requirement to consider persistence. For this requirement, known materials were identified by class and tests were specified to measure these materials as a separate section of the regulations. Thus, initially, heavy metals, halogenated organic compounds, and aromatic hydrocarbons were designated as persistent and potentially having genetic effects.

[25] WAC 173-303-070(5)(a)

In order to avoid regulating low concentrations, it was decided that wastes must contain a certain concentration of polycyclic aromatic hydrocarbons (PAH) or halogenated organic compounds (HOC) would be subject to persistence criteria. For PAHs, the waste would designate as DW if the total concentration of PAHs in the waste is greater than 1.0 percent by weight of the waste (10,000 ppm). For halogenated organic compounds (HOC), the waste would designate as DW if the total concentration of HOC in the waste exceeds 100 ppm (greater than 0.01 percent). When a waste has greater than 1.0 percent HOC content (10,000 ppm), the waste is then considered EHW.

B. ACUTE TOXICITY

B.1 Introduction

Both acute fish and mammalian toxicity are an index of acute biological hazard. Although acute toxicity criteria have been identified as biological in nature, generators may also choose to use chemical testing if the constituents of the waste stream are known. In this circumstance, chemical tests are valuable in determining the chemical concentration, which can be used in referencing levels of toxicity for book designation.

B.2 Acute Toxicity Criteria

Generators can choose to book designate wastes for toxicity, use chemical tests in conjunction with book designation, or biologically test the waste for toxicity.

When a generator chooses to book designate waste, he/she must follow the book designation procedure as outlined in WAC 173-303-100(5)(b). Book designation is a very common procedure for toxic wastes.[26] To book designate a waste, the generator applies existing knowledge of the various chemical constituents of the waste stream. This knowledge could be gained using a combination of tools such as Material Safety Data Sheets (MSDSs) for incoming chemicals, an understanding of reaction, concentration, or dilution effects associated with use of the chemicals in the production process, and supplemented (if necessary) with testing data. Pursuant to WAC 173-303-070(4), however, Ecology could require testing if there is reason to believe a waste has been improperly designated.

The generator could choose to determine the actual concentration of the various chemicals in the waste stream using any of the approved test methods as listed under WAC 173-303-110. Once this chemical information is acquired, the generator is required to determine the toxic category

[26] Under the Model Toxics Control Act (MTCA), wastes may be chemically tested to determine if the MTCA cleanup levels have been met or to designate a waste.

for each known constituent. The toxic category for each constituent may be determined by obtaining data from The National Institute for Occupational Safety and Health's (NIOSH) Registry of Toxic Effects of Chemical Substances (RTECS).[27]

The generator may choose to test the waste according to *Biological Testing Methods,* WDOE #80-12, the most recent revision, instead of using the book designation procedure. Any of these procedures are accepted in Washington State for designating wastes as toxic dangerous waste.

C. PERSISTENCE (CHRONIC TOXICITY)

C.1 Introduction

Organic compounds, such as heating and motor fuels, cleaning solvents, paints, varnishes, and aerosols are very commonplace materials. From a safety perspective, the principal hazards of organic compounds is that they are frequently toxic, flammable, and/or may achieve explosive limits in the air. From an environmental perspective, the primary hazard of organic compounds is their ability to cause a range of detrimental chronic health effects. This hazard, combined with an organic compound's ability to persist in the environment has led to regulatory standards in Chapter 173-303 WAC.

C.1.a Definition of Persistence

In Washington State, a waste designates as a dangerous waste if it meets the definition of persistence. "Persistence" means the quality of a material which, as defined in WAC 173-303-040, retains more than half of its initial activity after one year (365 days) in either a dark anaerobic or dark aerobic environment at ambient conditions.[28] Generators are not required analyze a waste to determine whether it retains more than half of its initial activity after one year (365 days). Instead, generators are required to identify specific persistence compounds. Those persistence compounds are either halogenated organic compounds (HOC) or polycyclic aromatic hydrocarbons (PAH). Chapter 173-303 WAC identifies these two classes of persistent organic chemical compounds due to the fact that they present a long-term threat because of bioaccumlulation or present a chronic threat to human health and the environment.

[27] Other published data, such as Hazardous Substances Data Base, with the same information as RTECS can be I used if the toxicity information cannot be found in RTECS.
[28] WAC 173-303-040

C.1.b Definition of Halogenated Organic Compounds (HOC)

For the purposes of WAC 173-303-040, HOC means any organic compound which includes at least one atom of either fluorine, bromine, chlorine, or iodine which is/are bonded directly to a carbon atom. The carbon-halogen bond is one of the primary organic structures that resist biodegredation in the environment. Some examples of chemicals not intended to be regulated as HOC are the hydrochlorides, the sulfonyl chlorides, and other classes of compounds where the halide is not bound to a carbon atom. Also, HOCs which are polymerized, or chemically bound in a solid matrix are not subject to regulation under WAC 173-303-100. An example of polymerized or chemically bound HOCs is PVC pipe.

C.1.c **Definition of Polycyclic Aromatic Hydrocarbons (PAH)**

"Polycyclic aromatic hydrocarbons" is a class of chemicals that is clearly defined in both chemical and regulatory terms. PAHs are clearly defined by the regulations through a specific list of chemical constituents of concern. For the purposes of WAC 173-303-040, PAH means those hydrocarbon molecules composed of two or more fused benzene rings. There axe twenty PAHs of concern under current Dangerous Waste Regulations. They are:

Acenaphthene	Dibenzo(a,h)anthracene
Acenaphthylene	Dibenzo(a,e)pyrene
Anthracene	Dibenzo(a,h)pyrene
Benzo(a)anthracene	Diberizo(a,i)pyrene
B enzo(a)pyrene	Dibenzo(a,1)pyrene
Benzo(b)fluoranthene	Fluoranthene
Benzo(g,h,i)perylene	Fluorene
Benzo(k)fluoranthene	Indeno(1,2,3-c,d)pyrene
Chrysene	Phenanthrene
Dibenzo(aj) acndine	Pyrene

C.2 Test Methods for Determining HOC

When a waste contains one or more halogenated organic compounds, the total HOC concentration must be determined by summing the concentration percentages for all of the identified halogenated compounds. If the total concentration of HOC exceeds 100 ppm,[29] the waste would then designate as DW. If the total concentration of HOC exceeds 10,000 ppm, the waste would then designate as an extremely hazardous waste (EHW).[30]

It is very important that generators understand that both volatile and semi-volatile halogenated organic compounds may cause a waste to designate as persistent waste. Unfortunately, there doesn't exist a single determinative method that will clearly identify all potential HOC that would be of concern in Washington State.

It is also important to note that other sections of Chapter 173-303 WAC contain requirements for I', halogenated compounds. For example, the toxicity characteristics[31] list contains twenty-three halogenated (chlorinated) compounds, over fifty percent of the forty-three substances to be determined under TCLP. Under WAC 173-303-9904, spent halogenated solvents are identified in the "F" list. In WAC 173-303-515, used oil when burned for energy recovery is presumed to be dangerous waste if it contains more than 1,000 ppm total halogens. However, it is important to note that, under most circumstances, a waste that is not identified as dangerous waste under any of these characteristics, lists, or other criteria must still be considered for testing under the halogenated organic compound testing methods described below if the waste is an unknown or if Ecology has invoked WAC 173-303-070(4).

Because of the wide scope of potentially halogenated wastes streams produced by generators, Ecology recommends that the generator rely on their analytical laboratory for the appropriate analytical method to determine the HOC content in their specific waste stream.

The following test methods are recommended for use in the determination of whether a waste would designate under the criteria of persistence, HOC. Please note that SW-846 contains many methods not mentioned in this document that could satisfy the requirements of this chapter. If a generator knows or suspects the constituents in their waste stream would not be identified by the methods specified below, they must consult their analytical laboratory for the appropriate test method.

C.2.a Screening Methods for Determining HOC

The concentration levels for HOC are based on the whole compound; both the organic base and the associated halogen portion. Halogens can be substituted on an organic base from 0.01 percent to 90 percent. Ecology has determined a need for guidance on designating a waste using the halogen portion of the HOC, only.

[29] ppm: parts per million
[30] WAC 173-303-100(6)
[31] See Chapter 2 Dangerous Waste Characteristics D.

C.2. a.1 HOC's ***as Halogens***

Ecology has conservatively chosen a concentration value that is 10 % of the current regulatory thresholds for designation of a persistent HOC dangerous waste for determining the total concentration level for HOCs as halogens.

Ten percent was chosen based on WAC 173-303-515, *Special requirements for used oil burned for energy recovery.* In this rule, there is a rebuttable standard of 1000 ppm total halogens that determines whether a used oil has been mixed with a halogenated dangerous waste. This level is exactly 10 % of the current 10,000 ppm standard for EHW HOC.

The *Special requirements for used oil burned for energy recovery* rule was chosen as representative due to the type of waste streams that are currently being designated as persistent waste. They are:

- halogenated solvent solids
- grease
- solids contaminated with grease
- tar and heavy petroleum distillates
- waste and used oils
- used solvent
- used oil contaminated with 1,1,1-trichloroethane
- parts washer solvent

Most of these wastes are typical of the types of wastes that go for fuel blending. Therefore, the concentration levels for HOCs were matched with the concentration level that has been established for total halogens in waste oils.

C.2.a.2Screenihg Criteria for *HOC's as Halogens*

Ecology recommends the following **screening criteria,** which can be used to determine if a waste designates as a HOC based on the total halogen content of the waste stream.

The following criteria must be followed to properly determine waste properties under the screening method:

1. Determine the total concentration of halogens in the waste stream. If the waste contains a total halogen:

Concentration level of. . .	Then your waste's designation, and waste # are. . .
10 ppm to 1000 ppm	DW, WP02
greater than 1000 ppm	EHW, WPOl

2. Wastes containing halogens at the concentration levels specified are presumed to be a dangerous waste because those halogens are organic. Persons may rebut this presumption if

   a) The generator can demonstrate that a portion of the total concentration level of halogens is due to inorganic halogens, thereby changing the actual total concentration level of halogens that are organic.

   b) The generator uses higher determinative methods, such as SW-846 Method 826013, for volatile organics, and SW-846 Method 8270C, for semi-volatile organics, to determine the actual total concentration level of HOC.

      - If the generator demonstrates that the total concentration level of HOC is less than 100 ppm, they will have successfully rebutted the organic halogen presumption and the waste would then be non-dangerous for HOC. (See Example 3-1)

      - If the generator demonstrates that the total concentration level of HOC is less than 10,000 ppm, they may designate the waste as DW, instead of EHW for HOC.

2. If the generator has knowledge of the specific halogenated compounds present in the waste, they should be able to calculate the quantity of HOC, as in the example for HOC.

EXAMPLE 3-1:

HOC's as Halogens Calculation

Using the example of chlorophenol, Method 9076 reports in mg/kg of chlorine while Method 8270C reports mg/kg of chlorophenol. In the case of a known compound like chlorphenol, if Method 9076 reported 27.58 mg/kg of chlorine, Method 8270C would report 100 mg/kg of chlrophenol. This result is calculable, since we know the percentage of chlorine in that molecule.

If chlorophenol was the only chlorinated compound contributing halogens to the waste stream, the generator could not rebut the Method 9076 result to support the determination of a waste being non-dangerous. They would have to designate this waste as DW based on the result of 100 mg/kg (ppm) from either the GC/MS analysis or the calculated result.

Other factors, such as inorganic halides in the waste stream, could change this determination through a successful rebuttal.

C.2.a.3Screening Methods

Ecology recommends that *SW-846* Method *9076* be used as the screening method in the determination of total halogens in a waste stream. Method *9076* is the test method for Total Chlorine in New and Used Petroleum Products by Oxidative Combustion and Microcoulometry. Although the title of this test method implies that only petroleum products are analyzed, this method has an optional sample introduction procedure, allowing soil and liquid samples to be analyzed as well. Ecology recognizes the following interferences with Method *9076:*

1. Method *9076* does not detect all halogens specified under the definition of HOC. This method only quantifies the chlorine, half of the bromine, half of the iodine, and none of the fluorine. i

2.1This method may experience positive interferences from inorganic halides.

Because Ecology supports the use of Method 9076 as a screening method for HOC, it has been included in Appendix 3.

Although Ecology supports the use of SW-846 Method 9076 for the determination of HOC's as halogens, it is recognized that there exists several halogen specific analyses that could satisfy the screening criteria. Table 3-1: Methods for Determining Halogens, lists some of the analysis described in SW-846.

TABLE 3-1:Screening Methods for Halogenated Organic Compounds

Method No.	Method Title
Method 9075	Test Method for Total Chlorine in New and Used Petroleum Products b X-Ray Fluorescence Spectrometry (XRF)
Method 9076	Test Method for Total Chlorine in New and Used Petroleum Products b Oxidative Combustion and Microcoulometry
Method 9077	Test Methods for Total Chlorine in New and Used Petroleum Products (Field Test Kit Methods).
Method 9211	Potentiometric Determination of Bromide in Aqueous Samples with Ion-Selective Electrode
Method 9212	Potentiometric Determination of Chloride in Aqueous Samples with Ion-Selective Electrode
Method 9214	Potentiometric Determination of Fluoride in Aqueous Samples with Ion-Selective Electrode
Method 9250	Chloride (Colorimetric, Automated Ferricyanide AAI)
Method 9251	Chloride (Colorimetric, Automated Ferricyanide AAII)
Method 9253	Chloride (Titrimetric, Silver Nitrate)

C.2.b Determinative Methods for HOC

Ecology recommends that the following criteria be followed to properly determine appropriate **determinative methods** for HOC waste properties:

1. If the chemical constituents of the waste stream are unknown, the generator should test the waste using both Method 8260B, for the volatile HOC portion of the waste, and Method 8270C, for the semi-volatile HOC portion of the waste. Tentatively identified compounds (TIC) are peaks with a response greater than 10% of the nearest internal standards response. The largest 20 TIC's for Methods 8260B and 8270C are to be reported along with those constituents positively identified by these methods. The sum of the halogenated organic compounds detected from these methods can then be used to designate the waste. Note that these methods give the widest range of

analytes detected in the `8000 series' of determinative analyses. Ecology acknowledges that not all HOCs will be captured by these two methods.

2. If the chemical constituents of the waste stream are known, the generator must consult with their analytical laboratory to determine which test method will sufficiently determine the HOC content of their waste stream. Ecology recommends the use of the `8000 series' methods in SW-846. As with all of the 8000 series methods, e.g. 8021B and 8121, specific analytes are targeted. Although these methods have a limited target list associated with them, other compounds not listed may be able to be determined using these methods.

TABLE 3-2:Determinative Methods for Halogenated Organic Compounds

SW-846 Test Method Number	Analytes Detected	Comments
8021B	Halogenated Volatiles	This method does not have as extensive a list of target compounds as 8260.
8081A	Organochlorine Pesticides method.	This method will detect PCBs, although PCBs are not target compounds of this
8082	PCBs	This method will detect Organochlorine Pesticides, although Organochlorine Pesticides are not target compounds of this method.
8111	Haloethers	
8121	Chlorinated Hydrocarbons constituents.	This method will not capture all . potential chlorinated hydrocarbon
8151A	Chlorinated Herbicides	If a generator suspects that the waste is contaminated by compounds such as 2,4-D or Pentachlorophenol, this method would be appropriate for determining HOC for that waste stream.
8260B	Volatile Organic Compounds	This method will cover the widest range of volatile HOC of all the GC methods.
9270C	Semivolatile Organic Compounds	This method will cover the widest range of semi-volatile HOC of all the GC methods.

Since there are thousands of halogenated compounds potentially regulated under the regulatory definition of HOC, **there does not exist one single determinative method that will sufficiently capture all of the possible halogenated organic compounds in a waste stream.** It is only when a generator has sufficient knowledge of the waste that a specific analytical method can be applied to the waste stream. If the contents of the waste stream are unknown, there are potentially thirty methods in SW-846 that could be used for the determination of organic halides. These analyte specific methods would not capture all the various halogenated organic compounds which may possibly be present. Ecology recognizes that it is cost prohibitive to require the use of every available method in determining HOC content of a waste stream. Table 3-2 describes some of the organic test methods available for the determination of HOC.

C.3 Test Methods for Determining PAHs

PAHs are clearly defined by the regulations through a specific list of chemical constituents of concern. As with HOC, the total concentration of PAH must be determined by summing the concentration of each of the polycyclic aromatic hydrocarbons that have been quantified by one of the methods listed below. If the total concentration of PAHs exceeds 10,000 ppm, the waste would then designate as an extremely hazardous waste (EHW). There is no DW concentration level for PAHs.

C.3.a SW-846 Method 8100

Method 8100 is the test method for Polynuclear Aromatic Hydrocarbons. Method 8100 is a packed column method, but capillary columns are allowed to be substituted. Although this test method will detect all fifteen chemical compounds listed under the definition of PAHs, this method has a tendency to produce results biased high due to chromatographic interferences.

Since this method employs FID (flame ionization detection) which is basically a "universal" detector, (e.g. responds to most organic compounds regardless of chemical structure or molecular elemental composition), any organic compound which elutes from the column at the same time as the compounds of interest would be interpreted as the compound of interest.

C.3.b SW-846 Method 8310

Method 8310 is the test method for Polynuclear Aromatic Hydrocarbons using High Pressure Liquid Chromatography (HPLC). This method, also, has a tendency to produce false high results, but has the ability to better differentiate between PAH pairs that might go unresolved in Method 8100. As the list of PAHs are so specific in the regulation, **Method 8310 is a better method for distinguishing 4-, 5-, and 6-ring compounds in the waste matrix.** Ecology recommends the use of Method 8310, preferential to Method 8100.

C.3.c SW-846 Method 8270C

Method 8270C is the test method for Semivolatile Organic Compounds by GC/MS. This method will detect all fifteen compounds and is the most accurate of the `8000 series' methods available to detect PAHs. The GC/MS techniques have the ability to "look through" the interferences and determine how much of the peak is the target compound. These methods also have some limitations, particularly if sufficient interferences are present to preclude obtaining a spectral match/identification of the target to the instrumental library. Although Method 8270C is the most expensive analysis of the three methods listed; **Ecology strongly recommends the use of Method 8270C,** preferential to Method 8100 and Method 8310.

C.4 Regulatory Definition; Criteria of Persistence

For the purposes of WAC 173-303-100(6), persistent constituents are chemical compounds which are either halogenated organic compounds (HOC), or polycyclic aromatic hydrocarbons (PAH), as defined under WAC 173-303-040. Except as provided for in WAC 173-303-070(4) or (5), a person may determine the identity and concentration of persistent constituents by either applying knowledge of the waste or by testing the waste.

1. Except as provided in WAC 173-303-070(4), if a person knows only some of the persistent constituents in the waste, or only some of the constituent concentrations, and if the waste is undesignated for those known constituents or concentrations, then the waste is not designated for persistence under this section.

2. When a waste contains one or more halogenated organic compounds (HOC) for which the concentrations are known, the total halogenated organic compound concentration must be determined by summing the concentration percentages for all of the halogenated organic compounds for which the concentration is known.

3. A person whose waste contains polycyclic aromatic hydrocarbons (PAH) as defined in WAC 173-303-040, must determine the total PAH concentration by summing the concentration percentages of each of the polycyclic aromatic hydrocarbons for which they know the concentration.

4. A person whose waste contains halogenated organic compounds and/or polycyclic aromatic hydrocarbons must determine its designation from the persistent dangerous waste table or persistent dangerous waste criteria graph WAC 173-303-9907.

PERSISTENT DANGEROUS WASTE TABLE

If your waste contains . . .	At a total concentration level of . . .	Then your waste's designation, and waste #are
Halogenated Organic Compounds (HOC)	• 0.01 percent to 1.0 percent • greater than 1.0 percent	• DW, WP02 • EHW, WP01
Polycyclic Aromatic Hydrocarbons (PAH)	greater than 1.0 percent	EHW*, WP03

*No DW concentration level for PAH.

APPENDIX 1

GLOSSARY OF TERMS

Accuracy:	The degree of agreement of an analytical result with the true value. The accuracy of a result is affected by both systematic and random errors.
Analyte:	Denotes `that which is to be analyzed for' in chemical, but not physical or biological, determinations.
Analytical method:	Denotes a set of written instructions specifying an analytical procedure to be followed to obtain a numerical estimate of the concentration of an analyte.
Completeness:	A measure of the amount of useable data obtained from a project compared to the amount expected.
Constituent:	A chemically distinct component of a dangerous waste stream or mixture as per WAC 173-303-040.
Dangerous waste constituent:	Those constituents listed in WAC 173-303-9905 and any other constituents that have caused a waste to be a dangerous waste under Chapter 173-303 WAC.
Dangerous wastes:	Those solid wastes designated in WAC 173-303-070 through 173-303-100 as dangerous, or extremely hazardous or mixed waste. For the purposes of Chapter 173-303 WAC, the words "dangerous waste" will refer to the full universe of wastes regulated by this chapter. The abbreviation "DW" will refer only to that part of the regulated universe which is not extremely hazardous waste.
Designation:	The process completed to determine if a solid waste is a dangerous waste resulting in the assignment of proper federal and state waste codes.

Disposal:	The discharging, discarding, or abandoning of dangerous wastes or the treatment, decontamination, or recycling of such wastes once they have been discarded or abandoned. This includes the discharge of any dangerous wastes into or on any land, air, or water, as per WAC 173-303-040.
Equivalent test method:	A laboratory or field testing method used to determine a waste's characteristics or composition that has been approved by Ecology in accordance with Chapter 173-303 WAC in lieu of using a laboratory or field testing method required by the regulation. An equivalent test method can only be approved through a rulemaking petition to Ecology in accordance with WAC 173-303-110(5) and -.901(2).
Extremely hazardous waste:	Those dangerous and mixed wastes designated in WAC 173-303-100 as extremely hazardous. The abbreviation "EHW" will be used in Chapter 173-303 WAC to refer to those dangerous and mixed wastes which are extremely hazardous.
Generator:	Any person, by site, whose act or process produces dangerous waste or whose act first causes a dangerous waste to become subject to regulation, as per WAC 173-303-040.
Halogenated organic compound:	Any organic compounds which, as part of their composition, include one or more atoms of fluorine, chlorine, bromine, or iodine which is/are bonded directly to a carbon atom, as described in WAC 173-303-040.
Hazardous wastes:	Those solid wastes designated by 40 CFR Part 261, and regulated as hazardous and/or mixed waste by the United States EPA.
Ignitable waste:	A dangerous waste that exhibits the characteristic of ignitability described in WAC 173-303-090(5).
Leachate:	Any liquid, including any components suspended in the liquid, that has percolated through or drained from dangerous waste, as per WAC 173-303-040.

Appendix One - Glossary of Terms

NIOSH registry: The registry of toxic effects of chemical substances which is published by the National Institute for Occupational Safety and Health.

Organic/carbonaceous waste: A dangerous waste that contains combined concentrations of greater than ten percent organic/carbonaceous constituents in the waste. Organic/carbonaceous constituents are those substances that contain carbon-hydrogen, carbon-halogen, or carbon-carbon bonding, as defined in WAC 173-303-040.

Persistence: The quality of a material which , as defined in WAC 173-303-040, is either a halogenated organic compound (HOC) or a polycyclic aromatic hydrocarbon (PAH),and retains more than half of its initial activity after one year (365 days) in either a dark anaerobic or dark aerobic environment at ambient conditions.

Person: Any person, firm, association, country, public or municipal or private corporation, agency, or other entity whatsoever, as defined in WAC 173-303-040.

Pesticide: Means but is not limited to:

1. Any substance or mixture of substances intended to prevent, destroy, control, repel, or mitigate any insect, rodent, nematode, mollusk, fungus, weed, and any other form of plant or animal life, or virus (except virus on or in living man or other animal) which is normally considered to by a pest or which the department of agriculture may declare to be a pest;
2. Any substance or mixture of substances intended to be used as a plant regulator, defoliant, or desiccant;
3. Any substance or mixture of substances intended to be used as spray adjuvant;
4. Any other substance intended for such use as may be named by the department of agriculture by regulation; and
5. Herbicides, fungicides, insecticides, and rodenticides are pesticides for the purposes of Chapter 173-303 WAC.

Polycyclic aromatic hydrocarbons: Those hydrocarbon molecules composed of two or more fused benzene rings. For the purposes of Chapter 173-303 WAC, the PAHs of concern for designation are: Acenaphthene,acenaphthylene,fluorene, anthracene, fluoranthene, phenanthrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, pyrene, chrysene, benzo(a)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene, dibenzo[(a,e), (a,h), (a,i), and (a, l)]pyrenes, and dibenzo(a,j)acridine.

Process knowledge: Knowledge the generator applies to a solid waste to determine if it is a dangerous waste in light of the materials or the process used. Such knowledge can be used when the generator demonstrates the information to be sufficient for determining whether a solid waste is designated properly, as per WAC 173-303-070(3)(c)(ii).

Reactive waste: A dangerous waste that exhibits the characteristic of reactivity described in WAC 173-303-090(7).

Sludge: Any solid, semisolid, or liquid waste generated from a municipal, commercial, or industrial wastewater treatment plant, waste supply treatment plant, or air pollution control facility, as per 173-303-040. This term does not include the treated effluent from a wastewater treatment plant.

Solid acid waste: A dangerous waste that exhibits the characteristic of low pH under the corrosivity tests of WAC 173-303-090(6)(a)(iii).

Toxic: Having the properties to cause or to significantly contribute to death, injury, or illness of man or wildlife such as carcinogenicity, mutagenicity, or teratogenicity as per WAC 173-303-040.

Waste stream: Waste streams have an individual point of generation. Individual waste streams include:

1. Wastes that are physically or chemically different from each other;
2. Wastes that are generated from different types of processes; and
3. Wastes that are the same type, but are generated at different points along the same process or at different process locations.

APPENDIX 2

Department of Transportation (DOT) Regulations - 49 CFR

A. **Ignitable Liquids**

1. 49 CFR § 173.120 Class 3--Definitions

B. **Ignitable Compressed Gases**

1. 49 CFR § 173.115 Class 2, Divisions 2.1, 2.2, and 2.3--Definitions.

C. Oxidizers

1. 49 CFR § 173.127 Class 5, Division 5.1--Definition and assignment of packing groups.

2. 49 CFR § 173.128 Class 5, Division 5.2--Definitions and types.

D. **Explosives**

1. 49 CFR § 173.50 Class 1--definitions.
2. 49 CFR § 173.53 Provisions for using old classifications of explosives.
3. 49 CFR § 173.54 Forbidden explosives.
4. 49 CFR § 173.56 New explosives--definition and procedures for classification and approval.
5. 49 CFR § 173.57 Acceptance criteria for new explosives.

2.A.1 49 CFR § 173.120 CLASS 3--DEFINITIONS

(a) ***Flammable liquid***. For the purpose of this subchapter, a *flammable liquid* (Class 3) means a liquid having a flash point of not more than 60.5 degrees C (141 degrees F), or any material in a liquid phase with a flash point at or above 37.8 degrees C (100 degrees F) that is intentionally heated and offered for transportation or transported at or above its flash point in a bulk packaging, with the following exceptions:

(1) Any liquid meeting one of the definitions specified in § 173.115.

(2) Any mixture having one or more components with a flash point of 60.5 degrees C (141 degrees F) or higher, that make up at least 99 percent of the total volume of the mixture, if the mixture is not offered for transportation or transported at or above its flash point.

(3) Any liquid with a flash point greater than 35 degrees C (95 degrees F) which does not sustain combustion. A procedure for determining if a material sustains combustion when heated under test conditions and exposed to an external source of flame is provided in Appendix H of this part.

(4) Any liquid with a flash point greater than 35 degrees C (95 degrees F) and with a fire point greater than 100 degrees C (212 degrees F) according to ISO 2592.

(5) Any liquid with a flash point greater than 35 degrees C (95 degrees F) which is in a water-miscible solution with a water content of more than 90 percent by mass.

(b) *Combustible liquid.*

(1) For the purpose of this subchapter, a *combustible liquid* means any liquid that does not meet the definition of any other hazard class specified in this subchapter and has a flash point above 60.5 degrees C (141 degrees F) and below 93 degrees C (200 degrees F).

(2) A flammable liquid with a flash point at or above 38 degrees C (100 degrees F) that does not meet the definition of any other hazard class may be reclassed as a combustible liquid. This provision does not apply to transportation by vessel or aircraft, except where other means of transportation is impracticable. An elevated temperature material that meets the definition of a Class 3 material because it is intentionally heated and offered for transportation or transported at or above its flash point may not be reclassed as a combustible liquid.

(c) Flash point.

(1) Flash point means the minimum temperature at which a liquid gives off vapor within a test vessel in sufficient concentration to form an ignitable mixture with air near the surface of the liquid. It shall be determined as follows:

(i) For a homogeneous, single-phase, liquid having a viscosity less than 45 S . U. S . at 38 degrees C (100 degrees F) that does not form a surface film while under test, one of the following test procedures shall be used:

(A) Standard Method of Test for Flash Point by Tag Closed Tester, (ASTM D 56); or

(B) Standard Methods of Test for Flash Point of Liquids by Setaflash Closed Tester, (ASTM D 3278).

(ii) For a liquid other than one meeting all of the criteria of paragraph (c)(1)(i) of this section, one of the following test procedures shall be used:

(A) Standard Method of Test for Flash Point by Pensky--Martens Closed Tester, (ASTM D 93). For cutback asphalt, use Method B of ASTM D 93 or alternate tests authorized in this standard; or

(B) Standard Methods of Test for Flash Point of Liquids by Setaflash Closed Tester (ASTM D 3278).

(2) For a liquid that is a mixture of compounds that have different volatility and flash points, its flash point shall be determined as specified in paragraph (c)(1) of this section, on the material in the form in which it is to be shipped. If it is determined by this test that the flash point is higher than -7 degrees C (20 degrees F) a second test shall be made as follows: a portion of the mixture shall be placed in an open beaker (or similar container) of such dimensions that the height of the liquid can be adjusted so that the ratio of the volume of the liquid to the exposed surface area is 6 to one. The liquid shall be allowed to evaporate under ambient pressure and temperature (20 to 25 degrees C (68 to 77 degrees F)) for a period of 4 hours or until 10 percent by volume has evaporated, whichever comes first. A flash point is then run on a portion of the liquid remaining in the evaporation container and the lower of the two flash points shall be the flash point of the material.

(3) For flash point determinations by Setaflash closed tester, the glass syringe specified need not be used as the method of measurement of the test sample if a minimum quantity of 2 ml (0.1 ounce) is assured in the test cup.

(d) If experience or other data indicate that the hazard of a material is greater or less than indicated by the criteria specified in paragraphs (a) and (b) of this section, the Associate Administrator for Hazardous Materials Safety may revise the classification or make the material subject or not subject to the requirements of parts 170-189 of this subchapter.[32]

2.B.1 49 CFR § 173.115 CLASS 2, DIVISIONS 2.1, 2.2, and 2.3--DEFINITIONS

(a) *Division 2.1 (flammable gas).* For the purpose of this subchapter, a *flammable gas* (Division 2.1) means any material which is a gas at 20 degrees C (68 degrees F) or less and 101.3 kPa (14.7 psi) of pressure (a material which has a boiling point of 20 degrees C (68 degrees F) or less at 101.3 kPa (14.7 psi)) which-

I

(1) Is ignitable at 101.3 kPa (14.7 psi) when in a mixture of 13 percent or less by volume with air; or

(2) Has a flammable range at 101.3 kPa (14.7 psi) with air of at least 12 percent regardless of the lower limit.

Except for aerosols, the limits specified in paragraphs (a)(1) and (a)(2) of this section shall be determined at 101.3 kPa (14.7 psi) of pressure and a temperature of 20 degrees C (68 degrees F) in accordance with ASTM E681-85, Standard Test Method for Concentration Limits of Flammability of Chemicals or other equivalent method approved by the Associate Administrator for Hazardous Materials Safety. The flammability of aerosols is determined by the tests specified in § 173.306(i) or this part.

(b) *Division 2.2 (non-flammable, nonpoisonous compressed gas--including compressed gas, liquefied gas, pressurized cryogenic gas, compressed gas in solution, asphyxiant gas and oxidizing gas).* For the purpose of this subchapter, a non-flammable, non-poisonous compressed gas (Division 2.2) means any material (or mixture) which-

(1) Exerts in the packaging an absolute pressure of 280 kPa (41 psia) or greater at 20 degrees C (68 degrees F), and

(2) Does not meet the definition of Division 2.1 or 2.3.

[32] [Amdt. 173-224, 55 FR 52634 Dec. 21, 1990, as amended by Amdt. 173-227, 56 FR 49989, Oct. 2, 1991; 56 FR 66268; Dec. 20, 1991; 57 FR 45461, Oct. 1, 1992; Amdt. 173-241, 59 FR 67506, 67507, Dec. 29, 1994]

(c) ***Division 2.3 (Gas Poisonous by inhalation).*** For the purpose of this subchapter, a *gas poisonous by inhalation* (Division 2.3) means a material which is a gas at 20 degrees C (68 degrees F) or less and a pressure of 101.3 kPa (14.7 psi) (a material which has a boiling point of 20 degrees C (68 degrees F) or less at 101.3 kPa (14.7 psi)) and which-

(1) Is known to be so toxic to humans as to pose a hazard to health during transportation, or

(2) In the absence of adequate data on human toxicity, is presumed to be toxic to humans because when tested on laboratory animals it has an LC50 value of not more than 5000 ml/m3 (see § 173.116(a) of this subpart for assignment of Hazard Zones A, B, C or D). LC50 values for mixtures may be determined using the formula in § 173.133(b)(1)(i) of this subpart.

(d) ***Non-liquefied compressed gas***. A *non-liquefied compressed gas* means a gas, other than in solution, which in a packaging under the charged pressure is entirely gaseous at a temperature of 20 degrees C (68 degrees F).

(e) ***Liquefied compressed gas***. A *liquefied compressed gas* means a gas which in a packaging under the charged pressure, is partially liquid at a temperature of 20 degrees C (68 degrees F).

(f) ***Compressed gas in solution***. A *compressed gas in solution is* a non-liquefied compressed gas which is dissolved in a solvent.

(g) Cryogenic liquid. A *cryogenic liquid* means a refrigerated liquefied gas having a boiling point colder than -90 degrees C (-130 degrees F) at 101.3 kPa (14.7 psi) absolute. A material meeting this definition is subject to requirements of this subchapter without regard to whether it meets the definition of a non-flammable, non-poisonous compressed gas in paragraph (b) of this section.

(h) ***Flammable range***. The term *flammable range* means the difference between the minimum and maximum volume percentages of the material in air that forms a flammable mixture.

(i) Service pressure. The term *service pressure* means the authorized pressure marking on the packaging. For example, for a cylinder marked "DOT 3A1800," the service pressure is 12410 kPa (1800 psi).

(j) Refrigerant gas or Dispersant gas. The terms *Refrigerant gas of Dispersant gas* apply to all non-poisonous refrigerant gases, dispersant gases (fluorocarbons) listed in §§ 172.101, 173.304(a)(2), 173,314(c), 173.315(a)(1) and 173.315(h), and mixtures thereof, or any other compressed gas having a vapor pressure not exceeding 1792 kPa

(260 psi) at 54 degrees C (130 degrees F), and restricted for use as a refrigerant, dispersant or blowing agent.[33]

2.C.1 49 CFI § 173.127 CLASS 5, DIVISION 5.1--DEFINITION AND ASSIGNMENT OF PACKING GROUPS

(a) *Definition.* For the purpose of this subchapter, ***oxidizer*** (Division 5.1) means a material that may, generally by yielding oxygen, cause or enhance the combustion of other materials. A solid material is classed as a Division 5.1 material if, when tested in accordance with appendix F to this part, in either concentration tested, the mean burning time of the test mixture, is equal to or less than that of the average of the three tests with ammonium persulfate mixture. A liquid is classed as a Division 5.1 material by analogy to existing entries in the § 172.101 Table.[34]

2C.2 49 CFR § 173.128 CLASS 5, DIVISION 5.2--DEFINITIONS AND TYPES

(a) *Definitions.* For the purposes of this subchapter, *organic peroxide* (Division 5.2) means any organic compound containing oxygen (O) in the bivalent -0-0- structure and which may be considered a derivative of hydrogen peroxide, where one or more of the hydrogen atoms have been replaced by organic radicals, unless any of the following paragraphs applies:

(1) The material meets the definition of an explosive as prescribed in subpart C of this part, in which case it must be classed as an explosive;

(2) The material is forbidden from being offered for transportation according to § 172.101 of this subchapter or § 173 .21;

(3) The Associate Administrator for Hazardous Materials Safety has determined that the material does not present a hazard which is associated with a Division 5.2 material; or

(4) The material meets one of the following conditions:

(i) For materials containing no more than 1.0 percent hydrogen peroxide, the available oxygen, as calculated using the equation in paragraph (a)(4)(ii) of this section, is not more than 1.0 percent, or

[33] [Amdt. 173-224; 55 FR 52634, Dec. 21, 1990, as amended at 56 FR 66268, Dec. 20, 1991; 57 FR 45461, Oct. 1, 1992; Amdt. 173-236, 58 FR 50236, Sept. 24, 1993; Amdt. 173-234, 58 FR 51532, Oct 1, 1993; Amdt. 173-241, 59 FR 67506, Dec. 29, 1994]

[34] [Amdt. 173-224, 55 FR 52634 Dec. 21, 1990, as amended by Amdt. 173-234, 58 FR 51532, Oct. 1, 1993]

(ii) For materials containing more than 1.0 percent but not more than 7.0 percent hydrogen peroxide, the available oxygen, content (Oa) is not more than 0.5 percent, when determined using the equation:

$$O_a = 16\, x \sum_{i=1}^{k} \frac{n_i c_i}{m_i}$$

where, for a material containing k species of organic peroxides:

O(subscript a: which stands for available Oxygen) = percent Oxygen. n_i-number of -0-0- groups per molecule of the *i*th species c_i-concentration (mass percent) of the *i*th species m_i molecular mass of the *i*th species

(b) *Generic types.* Division 5.2 organic peroxides are assigned to a generic system which~~, consists of seven types. An organic peroxide identified by technical name in the Organic Peroxides Table in § 173,225 is assigned to a generic type in accordance with that Table. Organic peroxides not identified in the Organic Peroxides Table are assigned to generic types under the procedures of paragraph (c) of this section.

(1) Type A. Organic peroxide type A is an organic peroxide which can detonate or deflagrate rapidly as packaged for transport. Transportation of type A organic peroxides is forbidden.

(2) *Type B.* Organic peroxide type B is an organic peroxide which, as packaged for transport, neither detonates nor deflagrates rapidly, but can undergo a thermal explosion.

(3) *Type C.* Organic peroxide type C is an organic peroxide which, as packaged for transport, neither detonates nor deflagrates rapidly and cannot undergo a thermal explosion.

(4) Type D. Organic peroxide type D is an organic peroxide which-

(i) Detonates only partially, but does not deflagrate rapidly and is not affected by heat when confined;

(ii) Does not detonate, deflagrates slowly, and shows no violent effect if heated when confined; or

(iii) Does not detonate or deflagrate, and shows a medium effect when heated under confinement.

(5) Type E. Organic peroxide type D is an organic peroxide which neither detonates nor deflagrates and shows low, or no, effect when heated under confinement.

(6) Type F. Organic peroxide type F is an organic peroxide which will not detonate in a cavitated state, does not deflagrate, shows only a low, or no, effect if heated when confined, and has low, or no, explosive power.

(7) *Type G.* Organic peroxide type G is an organic peroxide which will not detonate in a cavitated state, will not deflagrate at all, shows no effect when heated under confinement, and shows no explosive power. A type G organic peroxide is not subject to the requirements of this subchapter for organic peroxides of Division *5.2* provided that it is thermally stable (self-accelerating decomposition temperature is 50 degrees C (122 degrees F) or higher for a 50 kg (100 pounds) package). An organic peroxide meeting all characteristics of type G except thermal stability and requiring temperature control is classed as a type F, temperature control organic peroxide.

(c) Procedure for assigning an organic peroxide to a generic type. An organic peroxide shall be assigned to a generic type based on-

(1) Its physical state (i.e., liquid or solid), in accordance with the definitions for liquid and solid in § 171.8 of this subchapter;

(2) A determination as to its control temperature and emergency temperature, if any, under the provisions of § 173.21(f); and II

(3) Performance of the organic peroxide under the test procedures specified in the United Nations Recommendations on the Transport of Dangerous Goods, Tests and Criteria, part III, and the provisions of paragraph (d) of this section.

(d) Approvals.

(1) An organic peroxide must be approved, in writing, by the Associate Administrator for Hazardous Materials Safety, before being offered for transportation or transported, including assignment of a generic type and shipping description, except for-

(i) An organic peroxide which is identified by technical name in the Organic Peroxides Table in § 173.225(b);

(ii) A mixture of organic peroxides prepared according to § 173.225(c)(5); or

(iii) An organic peroxide which may be shipped as a sample under the provisions of § 173.225(c).

(2) A person applying for an approval must submit all relevant data concerning physical state, temperature controls, and tests results or an approval issued for the organic peroxide by the competent authority of a foreign government.

(e) Tests. The generic type for an organic peroxide shall be determined using the testing protocol from Figure 11.1 (Classification and Flow Chart Scheme for Organic Peroxides) from the UN Recommendations, Tests and Criteria, part Ill.[35]

2.D.1 49 CFR § 173.50 CLASS 1--DEFINITIONS

(a) Explosive. For the purpose of this subchapter, an **explosive** means any substance or article, including a device, which is designed to function by explosion (i.e., an extremely rapid release of gas and heat) or which, by chemical reaction within itself, is able to function in a similar manner even if not designed to function by explosion, unless the substance or article is otherwise classed under the provision of this subchapter.

(b) Explosives in Class 1 are divided into six divisions as follows:

(1) ***Division*** **1.1** consists of explosives that have a mass explosion hazard. A mass explosion is one which affects almost the entire load instantaneously.

(2) ***Division*** **1.2** consists of explosives that have a projection hazard but not a mass explosion hazard.

(3) Division 1.3 consists of explosives that have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard.

*(4****) Division 1.4*** consists of explosives that present a minor explosion hazard. The explosive effects are largely confined to the package and no projection of fragments of appreciable size or range is to be expected. An external fire must not cause virtually instantaneous explosion of almost the entire contents of the package.

(5) ***Division*** **1.5** consists of very insensitive explosives. This division is comprised of substances which have a mass explosion hazard but are so insensitive that there is very little probability of initiation or of transition from burning to detonation under normal conditions of transport.

(6) ***Division 1.6*** consists of extremely insensitive articles which do not have a mass explosive hazard. This division is comprised of articles which contain only

[35] [Amdt. 173-224, 55 FR 52634, Dec. 21, 1990, as amended at 56 FR 66268, Dec. 20, 1991; Amdt. 173-234, 58 FR 51532, Oct. 1, 1993; Amdt. 173-241, 59 FR 67508, Dec. 29, 1994]

extremely insensitive detonating substances and which demonstrate a negligible probability of accidental initiation or propagation.[36]

2.D.2 49 CFR § 173.53 PROVISIONS FOR USING OLD CLASSIFICATIONS OF EXPLOSIVES

Where the classification system in effect prior to January 1, 1991, is referenced in State or local laws, ordinances or regulations not pertaining to the transportation of hazardous materials, the following table may be used to compare old and new hazard class names:

Current classification	Class name prior to Jan. 1, 1991
Division 1.1	Class A explosives.
Division 1.2	Class A or Class B explosives.
Division 1.3	Class B explosive.
Division 1.4	Class C explosives.
Division 1.5	Blasting agents.
Division 1.6	No applicable hazard class.

2.D.3 49 CFR § 173.54 FORBIDDEN EXPLOSIVES

Unless otherwise provided in this subchapter, the following explosives shall not be offered for transportation or transported:

(a) An explosive that has not been approved in accordance with § 173.56 of this subpart.

(b) An explosive mixture or device containing a chlorate and also containing:

(1) An ammonium salt, including a substituted ammonium or quaternary ammonium salt; or

(2) An acidic substance, including a salt of a weak base and a strong acid.

(c) A leaking or damaged package of explosives.

(d) Propellants that are unstable, condemned or deteriorated.

(e) Nitroglycerin. diethylene glycol dinitrate, or any other liquid explosives not specifically authorized by this subchapter.

[36] [Amdt. 173-224, 55 FR 52617 Dec. 21, 1990, as amended at 56 FR 66267, Dec. 20, 1991]

(f) A loaded firearm (except as provided in 14 CFR 108.11).

(g) Fireworks that combine an explosive and a detonator.

(h) Fireworks containing yellow or white phosphorus.

(i) A toy torpedo, the maximum outside dimension of which exceeds *23* mm *(0.906* inch), or a toy torpedo containing a mixture of potassium chlorate, black antimony (antimony sulfide), and sulfur, if the weight of the explosive material in the device exceeds *0.26* g (0.01 ounce).

(j) Explosives specifically forbidden in the § 172.*101* Table of this subchapter.

(k) Explosives not meeting the acceptance criteria specified in § 173.*57* of this subchapter.

(1) An explosive article with its means of initiation or ignition installed, unless approved in accordance with § 173.*56.*

***2D.4 49 CFR* § 173.56** NEW EXPLOSIVES--DEFINITION AND PROCEDURES FOR CLASSIFICATION AND APPROVAL

(a) Definition of new explosive. For the purposes of this subchapter a *new explosive* means an explosive produced by a person who:

(1) Has not previously produced that explosive; or

(2) Has previously produced that explosive but has made a change in the formulation, design or process so as to alter any of the properties of the explosive. An explosive will not be considered a "new explosive" if an agency listed in paragraph (b) of this section has determined, and confirmed in writing to the

Associate Administrator for Hazardous Materials Safety, that there are no significant differences in hazard characteristics from the explosive previously approved.

(b) Examination, classing and approval. Except as provided in paragraph (j) of this section, no person may offer a new explosive for transportation unless that person has specified to the examining agency the ranges of composition of ingredients and compounds, showing the intended manufacturing tolerances in the composition of substances or design of articles which will be allowed in that material or device, and unless it has been examined, classed and approved as follows:

(1) A new explosive must be examined and assigned a recommended shipping description, class, and classification code by the Bureau of Explosives (BOE) or the Bureau of Mines, U.S. Department of Interior (BOM). The recommendation of class and classification code must be based on the tests and criteria prescribed in §§ 173.52, 173.57 and 173.58 of this subchapter. Each person requesting approval of a new explosive must submit a copy of the report of examination and assignment of recommended shipping description, class and classification code to the Associate Administrator for Hazardous Materials Safety for approval and must receive written approval and an EX-number from the Associate Administrator for Hazardous Materials Safety before offering that explosive for transportation.

(2) A new explosive made by or under the direction or supervision of a component of the DOD may be examined, classed, and concurred in by:

(i) U.S. Army Technical Center for Explosives Safety (SMCAC-EST), Naval Sea Systems Command (SEA-9934), or Air Force Safety Agency (SEW), when approved by the Chairman, DOD Explosives Board, in accordance with the Department of Defense Explosives Hazard Classification Procedures (TB 700-2, dated December 1989); or

(ii) The agencies and procedures specified in paragraph (b)(1) of this section.

(3) A new explosive made by or under the direction or supervision of the Department of Energy (DOE) may be-

(i) Examined by the DOE in accordance with the Explosives Hazard Classification Procedures (TB 700-2, dated December, 1989), and must be classed and approved by DOE; or

(ii) Examined, classed, and approved in accordance with paragraph (b)(1) of this section.

(4) For a material shipped under the description of "ammonium nitrate-fuel oil mixture (ANFO)", the only test required for classification purposes is the Cap Sensitivity Test (Test Method 5(a). prescribed in the Explosive Test Manual). The test must be performed by an agency listed in paragraph (b)(1), (b)(2), or (b)(3) of this section, the manufacturer, or the shipper. A copy of the test report must be submitted to the Associate Administrator for Hazardous Materials Safety before the material is offered for transportation, and a copy of the test report must be retained by the shipper for as long as that material is shipped. At a minimum, the test report must contain the name and address of the person or organization

conducting the test, date of the test, quantitative description of the mixture, including prill size and porosity, and a description of the test results.

(c) Filing **DOD or DOE** approval report. **DOD or DOE** must file a copy of each approval, accompanied by supporting laboratory data, with the Associate Administrator for Hazardous Materials Safety and receive acknowledgment in writing before offering the ' new explosive for transportation, unless the new explosive is:

(1) Being transported under paragraph (d) or (e) of this section; or

(2) Covered by a national security classification currently in effect. i

(d) Transportation of explosive samples for examination. Notwithstanding the requirements of paragraph (b) of this section with regard to the transportation of a new explosive that has not been approved, a person may offer a sample of a new explosive for transportation, by railroad, highway, or vessel from the place where it was produced to an agency identified in paragraph (b) of this section, for examination if-

(1) The new explosive has been assigned a tentative shipping description and class in writing by the testing agency;

(2) The new explosive is packaged as required by this part according to the tentative description and class assigned, unless otherwise specified in writing by the testing !, agency; and

(3) The package is labeled as required by this subchapter and the following is marked on the package:

(i) The words "SAMPLE FOR LABORATORY EXAMINATION";

(ii) The net weight of the new explosive; and

(iii) The tentative shipping name and identification number.

(e) Transportation of unapproved explosives for developmental testing. Notwithstanding the requirements of paragraph (b) of this section, the owner of a new explosive that has not been examined or approved may transport that new explosive from the place where it was produced to an explosives testing range if-

(1) It is not a primary (a 1.1A initiating) explosive or a forbidden explosive according to this subchapter;

(2) It is described as a Division 1.1 explosive (substance or article) and is packed, marked, labeled, described on shipping papers and is otherwise offered for

transportation in conformance with the requirements of this subchapter applicable to Division 1.1;

(3) It is transported in a motor vehicle operated by the owner of the explosive; and

(4) It is accompanied by a person, in addition to the operator of the motor vehicle, who is qualified by training and experience to handle the explosive.

(f) Notwithstanding the requirements of paragraphs (b) and (d) of this section, the Associate Administrator for Hazardous Materials Safety may approve a new explosive on the basis of an approval issued for the explosive by the competent authority of a foreign government, or when examination of the explosive by the Bureau of Explosives or the Bureau of Mines is impracticable, on the basis of reports of tests conducted by disinterested third parties, or may approve the transportation of an explosives sample for the purpose of examination by the BOE, the BOM, or other government agency.

(g) Notwithstanding the requirements of paragraph (b) of this section, an explosive may be transported under §§ 171.11, 171.12, 171.12a or § 176.11 of this subchapter without the approval of the Associate Administrator for Hazardous Materials Safety if the Associate Administrator for Hazardous Materials Safety has acknowledged, in writing, the acceptability of an approval issued by the competent authority of a foreign government pursuant to the provisions of the UN Recommendations, the ICAO Technical Instructions, the IMDG Code, or other national or international regulations based on the UN Recommendations. In such a case, a copy of the foreign competent authority approval, and a copy of the written acknowledgment of its acceptance must accompany each shipment of that explosive.

(h) The requirements of this section do not apply to cartridges, small arms which are:

(1) Not a forbidden explosive under § 173.54 of this subchapter;

(2) Ammunition for rifle, pistol, or shotgun;

(3) Ammunition with inert projectile or blank ammunition; and

(4) Ammunition not exceeding 50 caliber for rifle or pistol cartridges or 8 gauge for shotgun shells.

Cartridges, small arms meeting the criteria of this paragraph (h) may be assigned a classification code of 1.4S by the manufacturer.

(i) If experience or other data indicate that the hazard of a material or a device containing an explosive composition is greater or less than indicated according to the definition and criteria specified in §§ 173.50, 173.56, and 173.58 of this subchapter, the Associate Administrator for Hazardous Materials Safety may, following examination in accordance with paragraph (b) of this section, revise its classification or except the material or device from the requirements of this subchapter.

(j) Fireworks. Notwithstanding the requirements of paragraph (b) of this section, Division1.3 and 1.4 fireworks may be classed and approved by the Associate Administrator for Hazardous Materials Safety without prior examination and offered for transportation if the following conditions are met:

(1) The fireworks are manufactured in accordance with the applicable requirements in 'I APA Standard 87-1;

(2) A thermal stability test is conducted on the device by the **BOE, the BOM,** or the manufacturer. The test must be performed by maintaining the device, or a representative prototype of a large device such as a display shell, at a temperature of 75 degrees C (167 degrees F) for 48 consecutive hours. When a device contains more than one component, those components which could be in physical contact with each other in the finished device must be placed in contact with each other during the thermal stability test; and

(3) The manufacturer applies in writing to the Associate Administrator for Hazardous Materials Safety following the applicable requirements in APA Standard 87-1, and is notified in writing by the Associate Administrator for Hazardous Materials Safety that the fireworks have been classed, approved, and assigned an EX-number. Each application must be complete, including all relevant background data and copies of all applicable drawings, test results, and any other pertinent information on each device for which approval is being requested. The manufacturer must sign the application and certify that the device for which approval is requested conforms to APA Standard 87-1 and that the descriptions and technical information contained in the application are complete and accurate. If the application is denied, the manufacturer will be notified in writing of the reasons for the denial. The Associate Administrator for Hazardous Materials Safety may require that the fireworks be examined by an agency listed in paragraph (b)(1) of this section. 17

2.D.5 49 CFR § 173.57 ACCEPTANCE CRITERIA FOR NEW EXPLOSIVES

(a) Unless otherwise excepted, an explosive substance must be subjected to the Drop Weight Impact Sensitivity Test (Test Method 3(a)(i)), the Friction Sensitivity Test (Test Method 3(b)(iii)), the Thermal Stability Test (Test Method 3(c)) at 75 degrees C (167 degrees F) and the Small-Scale Burning Test (Test Method 3(d)(i)), each as described in the

[37] [Arndt. 173-224, 55 FR 52617 Dec. 21, 1990, as amended at 56 FR 66267, Dec. 20, 1991; Arndt. 173-234, 58 FR 51532, Oct. 1, 1993]

Explosive Test Manual (UN Recommendations on the Transport of Dangerous Goods, Tests and Criteria, Part I, Section Edition (see § 171.7 of this subchapter). A substance is forbidden for transportation if any one of the following occurs:

(1) For a liquid, failure to pass the test criteria when tested in the Drop Weight Impact Sensitivity Test apparatus for liquids;

(2) For a solid, failure to pass the test criteria when tested in the Drop Weight Impact Sensitivity Test apparatus for solids;

(3) The substance has a friction sensitiveness equal to or greater than that of dry pentaerythrite tetranitrate (PETN) when tested in the Friction Sensitivity Test;

(4) The substance fails to pass the test criteria specified in the Thermal Stability Test at 75 degrees C (167 degrees F); or

(5) Explosion occurs when tested in the Small-Scale Burning Test.

(b) An explosive article, packaged or unpackaged, or a packaged explosive substance must be subjected to the Thermal Stability Test for Articles and Packaged Articles (Test method 4(a)(i)) and the Twelve Meter Drop Test (Test Method 4(b)(ii)), when appropriate, in the Explosive Test Manual. An article or packaged substance is forbidden for transportation if evidence of thermal instability or excessive impact sensitivity is found in those tests according to the criteria and methods of assessing results prescribed therein.

(c) Dynamite (explosive, blasting, type A) is forbidden for transportation if any of the following occurs:

(1) It does not have uniformly mixed with the absorbent material a satisfactory antacide in a quantity sufficient to have the acid neutralizing power of an amount of magnesium carbonate equal to one percent of the nitroglycerin or other liquid explosive ingredient;

(2) During the centrifuge test (Test Method D-2, in appendix D to this part) or the compression test (Test Method D-3 in appendix D to this part), a nongelatin dynamite loses more than 3 percent by weight of the liquid explosive or a gelatin dynamite loses more than 10 percent by weight of the liquid explosive; or

(3) During the leakage test (Test Method D-1 in appendix D to this part), there is any loss of liquid.[38]

[38] [Amdt. 173-224, 55 FR 52617 Dec. 21, 1990, as amended at 58 FR 51532, Oct. 1, 1993]

APPENDIX 3

Analytical Methods for Designating Dangerous Waste

A. Sample Containers and Sample Preservation for Appendix 3 Analytical Methods

B. Analyses for the Ignitability Characteristic

  1. SW-846 Method 1010

  2. SW-846 Method 1020A

C. Analyses for the Corrosivity Characteristic

  1. SW-846 Method 9040B

  2. SW-846 Method 9045C

  3. SW-846 Method 1110

D. Analyses for the Reactivity Characteristic

  1. SW-846 Method 7.3.3.2

  2. SW-846 Method 7.3.4.2

  3. SW-846 Method 9014

  4. SW-846 Method 9034

E. Analysis for the Toxicity Characteristic

  1. SW-846 Method 1311

F. Analysis for the Criteria of Persistence: Halogenated Organic Carbon Screen

  1. SW-846 Method 9076

3.A Sample Containers and Sample Preservation

For the analysis in Appendix 3, the following chart contains information pertaining to sample containers and sample preservation:

Analysis		**Matrix**	**Container**	**Preservative**
SW-846	**Other methods**			
Method 1010: Flash Point (Pensky - Martens)	ASTM Standard D-93-79 or D-93-80	Solids greater than 20 glass jar percent by weight	glass jar	Cool to 4 degrees Celsius
Method 1020A: Flash Point (Setaflash)	ASTM Standard D-3278-78	Solids less than 20 percent by weight	glass jar	Cool to 4 degrees Celsius
Method 9040B: pH	• Standard Methods[1] 4500H • EPA Method' 150.1	Solids less than 20 percent by weight	glass jar or polyethylene	Cool to 4 degrees Celsius
Method 9045C: pH		Solids greater than 20 percent by weight	glass jar	Cool to 4 degrees Celsius
Method 1110: Corrosivity Towards Steel	NACE3 Standard TM-01-69	Aqueous and non-aqueous liquids	glass jar	Cool to 4 degrees Celsius
Method 7.3.3.2: Reactive Cyanide		Solids	glass jar	Cool to 4 degrees Celsius
Method 7.3.3.2: Reactive Cyanide	Standard Methods[33] 4500CN-C, 4500CN-E, and 450OCN-1	Aqueous liquids	amber polyethylene	• Cool to 4 degrees Celsius • NaOH to pH greater than 12 • Ascorbic acid

[1]*Standard Methods for the Examination of Water and Wastewater*, 18th Edition.
[2] *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*, EPA 600/4-79-020
[3] National Association of Corrosion Engineers

Analysis		**Matrix**	**Container**	**Preservative**
SW-846	**Other methods**			
Method 7.3.4.2: Reactive Sulfide		Solids	glass jar	Cool to 4 degrees Celsius
Method 7.3.4.2: Reactive Sulfide	• Standard Methods" 41 l OB • EPA Method34 150.1	Aqueous liquids	polyethylene	• Cool to 4 degrees Celsius • NaOH to pH greater than 9 • Zinc acetate
Method 1311: TCLP		Solids	glass jar	Cool to 4 degrees Celsius
Method 1311: TCLP		Aqueous and nonaqueous liquids	• 1 Liter HDPE bottle for metal analyses • 1 Liter glass jar for organic analyses	Cool to 4 degrees Celsius
Method 9076: Total Chlorine		Aqueous liquids, nonaqueous liquids, and solids	glass jar	Cool to 4 degrees Celsius
Method 8100: PAHs		Aqueous liquids, nonaqueous liquids, and solids	• 8 oz. glass jar (solids) • 1 gal. glass jar (liquids)	Cool to 4 degrees Celsius
Method 8310: PAHs		Aqueous liquids, nonaqueous liquids, and solids	• 8 oz. glass jar (solids) • 1 gal. glass jar (liquids)	Cool to 4 degrees Celsius
Method 8270C: Semivolatile organics	EPA Method 14 625	Aqueous liquids, nonaqueous liquids, and solids	• 8 oz. glass jar (solids) • 1 gal. glass jar (liquids)	Cool to 4 degrees Celsius

[33] *Standard Methods for the Examination of Water and Wastewater, 18th* Edition.
[34] *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater,* EPA 600/4-79-020

3.B.1 METHOD 1010

PENSKY-MARTINS CLOSED-CUP MPTHO IP FOR DETERMINING IGNITABILITY

1.0 SCOPE AND APPLICATION

1.1 Method 1010 uses the Pens -Mart6ns closed-cup tester to determine the flash point of liquids including those that tend to form a!, surface film under test conditions. Liquids containing non-filterable, suspended solids shall also be tested using this method.

2.0 SUMMARY OF METHOD

2.1 The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame ignites the vapor above the sample.

For further information on how to conduct a test by this method, see Reference 1 below.

3.0 METHOD PERFORMANCE

3.1 The Pensky-Martens and Set4flash Closed Testers were evaluated using five industrial waste mixtures and p-xylene. The results of this study are shown below in degrees F along with other data.

Sample	Pensky-Martens	Setaflash
12	143.7 ± 1.5	139.3 ± 2.1
22	144.7 ± 4.5	129.7 ± 0.6
32	93.7 ± 1.5	97.7 ± 1.2
42	198.0±4.0	185.3±0.6
52	119.3 ± 3.1	122.7 ± 2.5
p-xylene2	81.3 ± 1.1	79.3 ± 0.6
p-xylene3	77.7 ± O.5[a]	--
		--
Tanker oil	125, 135	
Tanker oil	180, 180	--
Tanker oil	110, 110	--
DIBK/xylene	102 ± [4b]	107

[a]12 determinations over five-day period.
[b]75/25 v/v analyzed by four laboratories.

4.0 REFERENCES

1. D 93-80, Test Methods for Flash Point by Pensky-Martens Closed Tester, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103, 04.09, 1986.

2. Umana, M., Gutknecht, W., Salmons, C., et al., Evaluation of Ignitability Methods (Liquids), EPA/600/54-85/053, 1985.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

3.B.2 METHOD 1020

SETAFLASH **CLOSED-CUP METHOD FOR DETERMINING IGNITABILITY**

1.0 SCOPE AND APPLICATION

1.1 Method 1020 makes use of the Setaflash Closed Tester to determine the flash point of liquids that have flash points between 0 degrees and 110 degrees C (32 degrees and 230 degrees F) and viscosities lower than 150 stokes at 25 degrees C (77 degrees F).

1.2 The procedure may be used to determine whether a material will or will not flash at a specified temperature or to determine the finite temperature at which a material will flash.

1.3 Liquids that tend to form surface films under test conditions or those that contain non-filterable suspended solids shall be tested for ignitability using Method 1010 (Pensky-Martens Closed-Cup).

2.0 SUMMARY OF METHOD

2.1 By means of a syringe, 2-mL of sample is introduced through a leak-proof entry port into the tightly closed Setaflash Tester or directly into the cup which has been brought to within 3 degrees C (5 degrees F) below the expected flash point.

2.2 As a flash/no-flash test, the expected flash-point temperature may be a specification (e.g., 60 degrees C). For specification testing, the temperature of the apparatus is raised to the precise temperature of the specification flash point by slight adjustment of the temperature dial. After 1 minute, a test flame is applied inside the cup and note is taken as to whether the test sample flashes or not. If a ,repeat test is necessary, a fresh sample should be used.

2.3 For a finite flash management, the temperature is sequentially increased through the anticipated range, the test flame being applied at 5 degrees C (9 degrees F) intervals until a flash is observed. A repeat determination is then made using a fresh sample, starting the test at the temperature of the last interval before the flash point of the material and making tests at increasing 0.5 degrees C (1 degrees F) intervals.

For further information on how to conduct a test with this method, see Reference 1 below.

3.0 METHOD PERFORMANCE

See Method 1010.

4.0 REFERENCES

1. D-3278-78, Test Method for Flash Point of Liquids by Setaflash Closed Tester, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

2. Umana, M., Gutknecht, W., Salmons, C., et al., Evaluation of Ignitability Methods (Liquids), EPA/600/54-85/053, 1985.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

3. C.1 METHOD 9040B

pH ELECTROMETRIC MEASUREMENT

1.0 SCOPE AND APPLICATION

1.1 Method 9040 is used to measure the pH of aqueous wastes and those multiphase wastes where the aqueous phase constitutes at least 20% of the total volume of the waste.

1.2 The corrosivity of concentrated acids and bases, or of concentrated acids and bases mixed with inert substances, cannot be measured. The pH measurement requires some water content.

2.0 SUMMARY

2.1 The pH of the sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. The measuring device is calibrated using a series of standard solutions of known pH.

3.0 INTERFERENCES

3.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or moderate (< 0.1 molar solution) salinity.

3.2 Sodium error at H levels > 10 can be reduced or eliminated by using a low-sodium-error electrode.

3.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by rinsing with distilled water. An additional treatment with hydrochloric acid (1:10) may be necessary to remove any remaining film.

3.4 Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference should be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. This error is sample-dependent and cannot be controlled. It should, therefore, be noted by reporting both the pH and temperature at the time of analysis.

4.0 APPARATUS AND MATERIALS

4.1 pH meter: Laboratory or field model. Many instruments are commercially available with various specifications and optional equipment.

4.2 Glass electrode.

4.3 Reference electrode: A silver-silver chloride or other reference electrode of constant potential may be used.

> NOTE: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

4.4 Magnetic stirrer and Teflon-coated stirring bar.

4.5 Thermometer and/or temperature sensor for automatic compensation.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Primary standard buffer salts are available from the National Institute of Standards and Technology (NIST) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.3 Secondary standard buffers may be prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions have been validated by comparison with NIST standards and are recommended for routine use.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples musts be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. (For corrosivity characterization, the calibration of the pH meter should include a buffer of pH 2 for acidic wastes and a pH 12 buffer for caustic wastes; also, for corrosivity characterization, the sample must be measured at 25±1°C if the pH of the waste is above 12.0.) Various instrument designs may involve use of a dial (to "balance" or "standardize") or a slope adjustment, as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar. If field measurements are being made, the electrodes may be immersed directly into the sample stream to an adequate depth and moved in a manner to ensure sufficient sample movement across the electrode-sensing element as indicated by drift-free readings (< 0.1 pH).

7.3 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

7.4 Thoroughly rinse and gently wipe the electrodes prior to measuring pH of samples. Immerse the electrodes into the sample beaker or sample stream and gently stir at a constant rate to provide homogeneity and suspension of solids. Note and record sample pH and temperature. Repeat measurement on successive aliquots of sample until values differ by < 0.1 pH units. Two or three volume changes are usually sufficient.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for the appropriate QC protocols.

8.2 Electrodes musts be thoroughly rinsed between samples.

9.0 METHOD PERFORMANCE

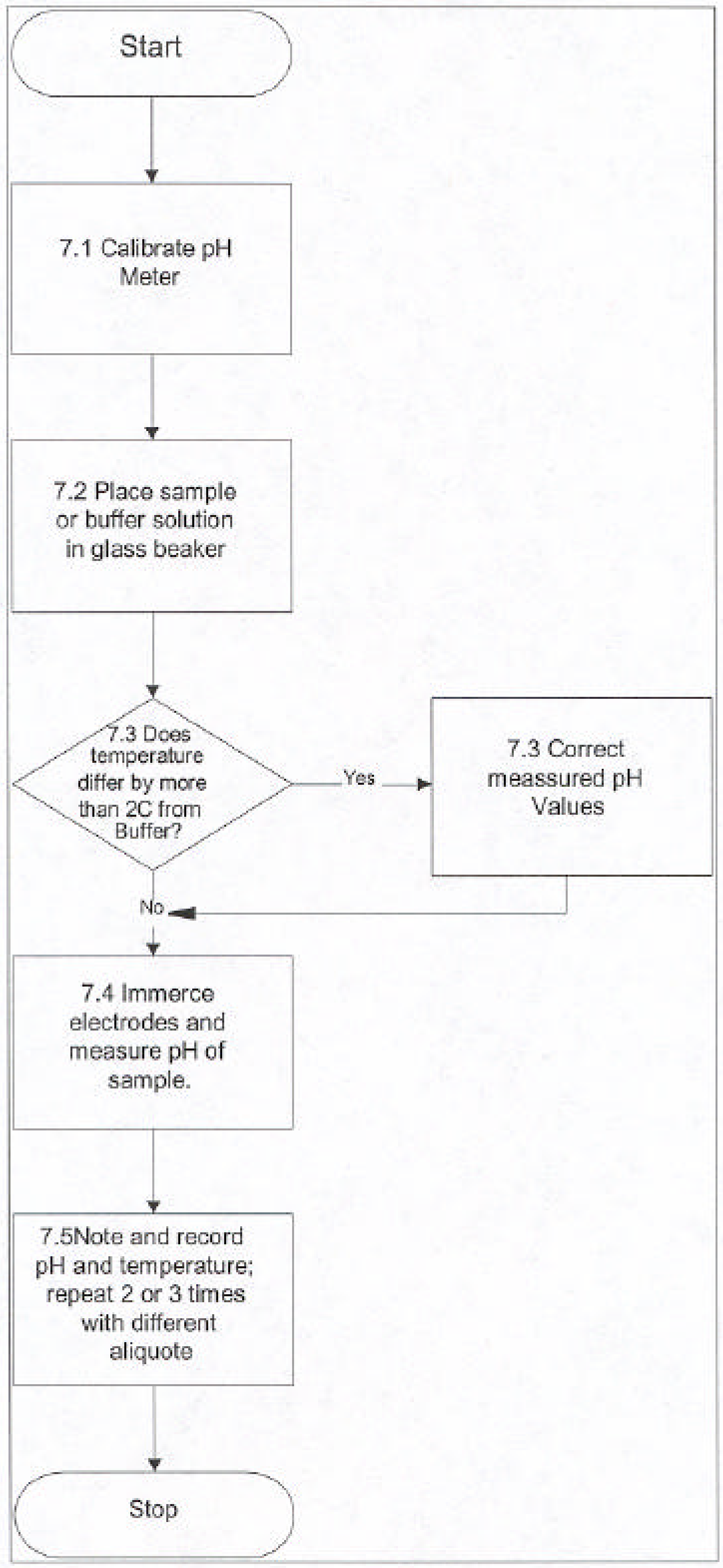
9.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

		Accuracy as	
	Standard Deviation	Bias	Bias
pH Units	pH Units	%	pH Unit
3.5	0.10	-01.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+ 1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

10.0 REFERENCES

1. National Bureau of Standards, Standard Reference Material Catalog 1986-87, Special Publication 260.

METHOD 9040B
pH ELECTROMETRIC MEASUREMENT



3. C.2 METHOD 9045C

SOIL AND WASTE pH

1.0 SCOPE AND APPLICATION

1.1 Method 9045 is an electrometric procedure for measuring pH in soils and waste samples. Wastes may be solids, sludges, or non-aqueous liquids. If water is present, it must constitute less than 20 % of the total volume of the sample.

2.0 SUMMARY OF METHOD

2.1 The sample is mixed with reagent water, and the pH of the resulting aqueous solution is measured.

3.0 INTERFERENCES

3.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of > 10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of < 1, may give incorrectly high pH measurements.

3.2 Temperature fluctuations will cause measurement errors.

3.3 Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can (1) be cleaned with an ultrasonic bath, or (2) be washed with detergent, rinsed several times with water, placed in 1:10 HC 1 so that the lower third of the electrode is submerged, and then thoroughly rinsed with water, or (3) be cleaned per the manufacturer's instructions.

4.0 APPARATUS AND MATERIALS

4.1 pH Meter with means for temperature compensation.

4.2 Glass Electrode.

4.3 Reference electrode: A silver-silver chloride or other reference electrode of constant potential may be used.

NOTE: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

4.4 Beaker: 50-mL.

4.5 Thermometer and/or temperature sensor for automatic compensation.

4.6 Analytical balance: capable of weighing 0.1 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Primary standard buffer salts are available from the National Institute of Standards and Technology (NIST) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.4 Secondary standard buffers may be prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions, which have been validated by comparison with NIST standards, are recommended for routine use.

6.0 SAMPLE PRESERVATION AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

Appendix Three - Analyses for the Corrosivity Characteristic - Method 9045C

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value. If an accurate pH reading based on the conventional pH scale [0 to 14 at 25°C] is required, the analyst should control sample temperature at 25±1°C when sample pH approaches the alkaline end of the scale (e.g., a pH of 11 or above).

7.2 Sample preparation and pH measurement of soils:

7.2.1 To 20 g of soil in a 50-mL beaker, add 20 mL of reagent water, cover, and continuously stir the suspension for 5 minutes. Additional dilutions are allowed if working with hygroscopic soils and salts or other problematic matrices.

7.2.2 Let the soil suspension stand for about 1 hour to allow most of the suspended clay to settle out from the suspension or filter or centrifuge off the aqueous phase for pH measurement.

7.2.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrodes into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.2.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values musts be corrected.

7.2.5 Report the results as "soil pH measured in water at __°C" where " __°C" is the temperature at which the test was conducted.

7.3 Sample preparation and pH measurement of waste materials:

7.3.1 To 20 g of waste sample in a 50-mL beaker, add 20 mL of reagent water, cover, and continuously stir the suspension for 5 minutes. Additional dilutions are allowed if working with hygroscopic wastes and salts or other problematic matrices.

7.3.2 Let the waste suspension stand for about 15 minutes to allow most of the suspended waste to settle out from the suspension or filter or centrifuge off aqueous phase for pH measurement.

NOTE: If the waste is hygroscopic and absorbs all the reagent water, begin the experiment again using 20 g of waste and 40 mL of reagent water.

NOTE: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned (Step 3.3) if it becomes coated with an oily material.

7.3.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant to establish good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrode into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.3.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.3.5 Report the results as "waste pH measured in water at _°C" where " °C" is the temperature at which the test was conducted.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for the appropriate QC protocols.
8.2 Electrodes must be thoroughly rinsed between samples.

9.0 METHOD PERFORMANCE

9.1 No data provided.

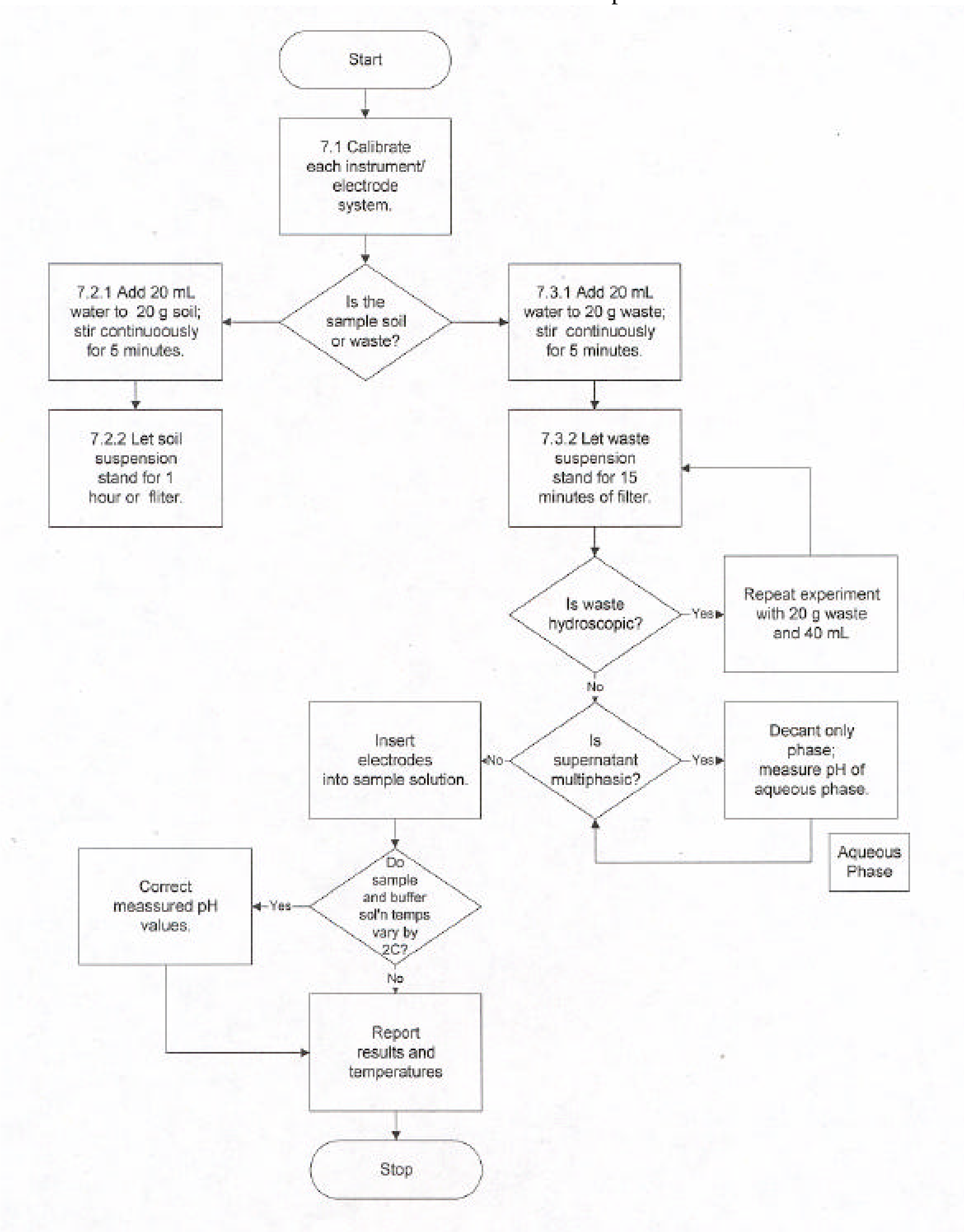
10.0 REFERENCES

1. Black, Charles Allen; Methods of Soil Analysis; American Society of Agronomy: Madison, WI, 1973.
2. National Bureau of Standards, Standard Reference Material Catalog, 1986-87, Special Publication 260.

Appendix Three - Analyses for the Corrosivity Characteristic - Method 9045C

METHOD 9045C

SOIL AND WASTE pH



3.C.3 METHOD 1110

CORROSIVITY TOWARD STEEL

1.0 SCOPE AND APPLICATION

1.1 Method 1110 is used to measure the corrosivity toward steel of both aqueous and nonaqueous liquid wastes.

2.0 SUMMARY OF METHOD

2.1 This test exposes coupons of SAE Type 1020 steel to the liquid waste to be evaluated and, by measuring the degree to which the coupon has been dissolved, determines the corrosivity of the waste.

3.0 INTERFERENCES

3.1 In laboratory tests, such as this one, corrosion of duplicate coupons is usually reproducible to within 10 percent. However, large differences in corrosion rates may occasionally occur under conditions where the metal surfaces become passivated. Therefore, at least duplicate determinations of corrosion rate should be made.

4.0 APPARATUS AND MATERIALS

4.1 An apparatus should be used, consisting of a kettle or flask of suitable size (usually 500 to 5,000 mL, a reflux condenser, a thermowell and temperature regulating device, a heating device (mantle, hot plate, or bath), and a specimen support system. A typical resin flask set up for this type of test is shown in Figure 1.

4.2 The supporting device and container shall be constructed of materials that are not affected by, or cause contamination of, the waste under test.

4.3 The method of supporting the coupons will vary with the apparatus used for conducting the test, but it should be designed to insulate the coupons from each other physically and electrically and to insulate the coupons from any metallic container or other device used in the test. Some common support materials include glass, fluorocarbon, or coated metal.

4.4 The shape and form of the coupon support should ensure free contact with the waste.

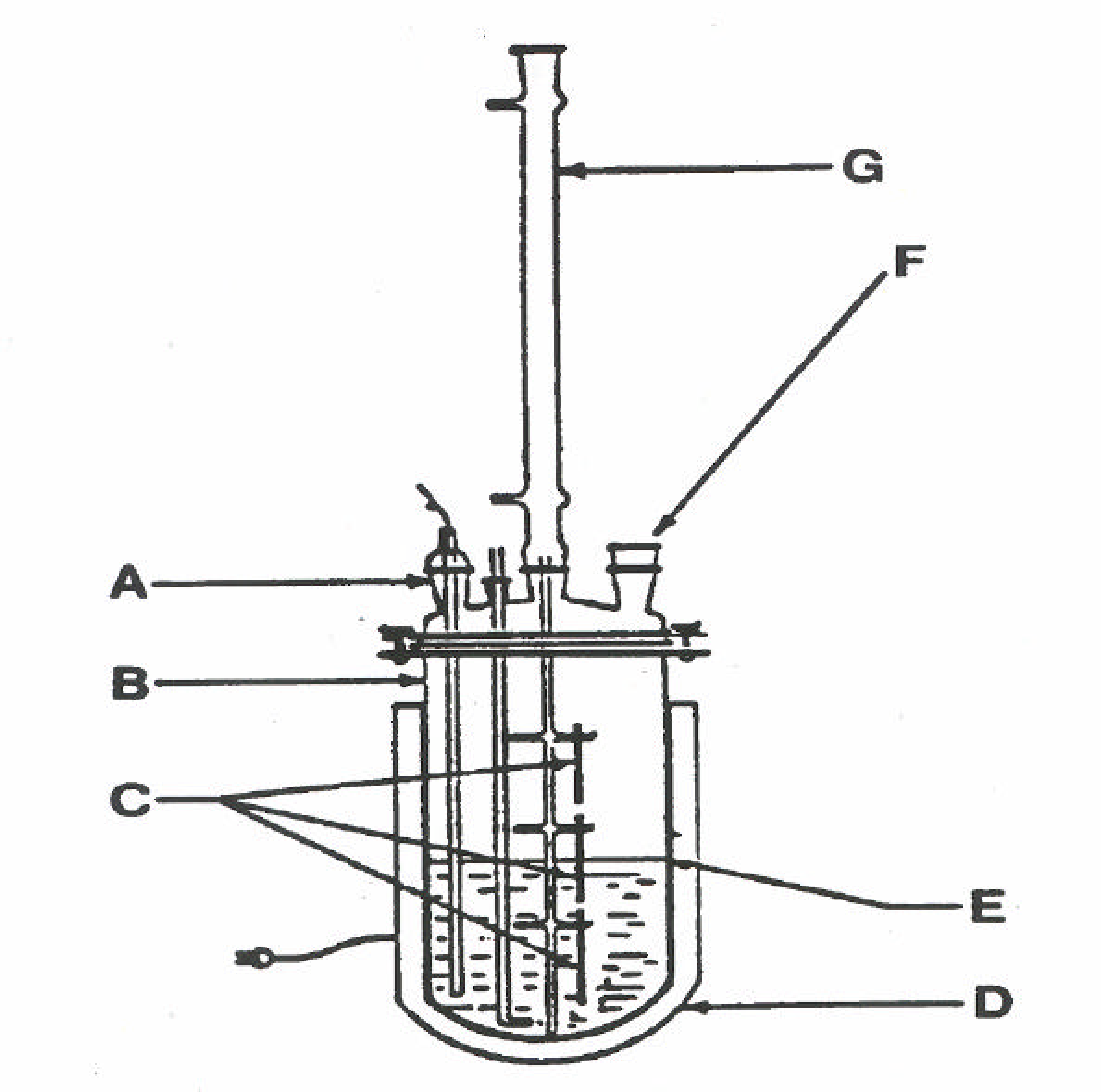


Figure 1. Typical resin flask that can be used as a versatile and convenient apparatus to conduct simple immersion tests. Configuration of the flask top is such that more sophisticated apparatus can be added as required by the specific test being conducted. A = thermowell, B = resin flask, C = specimens hung on supporting device, D = heating mantle, E = liquid interface, F = opening in flask for additional apparatus that may be required, and G = reflux condenser.

4.5 A circular specimen of SAE 1020 steel of about 3.75 cm (1.5 in.) diameter is a convenient shape for a coupon. With a thickness of approximately 0.32 cm (0.125 in.) and a 0.80-cm (0.4-in.)-diameter hole for mounting, these specimens will readily pass through a 45/50 ground-glass joint of a distillation kettle. The total surface area of a circular specimen is given by the following equation:

$$A = 3.14/2(D^2-d^2) + (t)(3.14)(D) + (t)(3.14)(d)$$

where:

t = thickness.
D = diameter of the specimen.
d = diameter of the mounting hole.

If the hole is completely covered by the mounting support, the last term in the equation, (t)(3.14)(d), is omitted.

4.5.1 All coupons should be measured carefully to permit accurate calculation of the exposed areas. An area calculation accurate to ±1 percent is usually adequate.

4.5.2 More uniform results may be expected if a substantial layer of metal is removed from the coupons prior to testing the corrosivity of the waste. This can be accomplished by chemical treatment (pickling), by electrolytic removal, or by grinding with a coarse abrasive. At least 0.254 mm (0.0001 in.) or 2-3 mg/cm2 should be removed. Final surface treatment should include finishing with #120 abrasive paper or cloth. Final cleaning consists of scrubbing with bleach-free scouring powder, followed by rinsing in distilled water and then in acetone or methanol, and finally by air-drying. After final cleaning, the coupon should be stored in a desiccator until used.

4.5.3 The minimum ratio of volume of waste to area of the metal coupon to be used in this test is 40 mL/cm2.

5.0 REAGENTS

5.1 Sodium hydroxide (NaOH), (20 percent): Dissolves 200 g NaOH in 800 mL Type II water and mix well.

5.2 Zinc dust.

5.3 Hydrochloric acid (HC1): Concentrated.

5.4 Stannous chloride ($SnC1_2$).

5.5 Antimony chloride ($SbC1_3$).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples should be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

7.0 PROCEDURE i

7.1 Assemble the test apparatus as described in Paragraph 4.0, above.

7.2 Fill the container with the appropriate amount of waste.

7.3 Begin agitation at a rate sufficient to ensure that the liquid is kept well mixed and homogeneous.

7.4 Using the heating device, bring the temperature of the waste to 55 degrees C (130 degrees F).

7.5 An accurate rate of corrosion is not required; only a determination as to whether the rate of corrosion is less than or greater than 6.35 mm per year is required. A 24 hr test period should be ample to determine whether or not the rate of corrosion is > 6.35 mm per year.

7.6 In order to determine accurately the amount of material lost to corrosion, the coupons have to be cleaned after immersion and prior to weighing. The cleaning procedure should remove all products of corrosion while removing a minimum of sound metal. Cleaning methods can be divided into three general categories: mechanical, chemical, and electrolytic.

7.6.1 Mechanical cleaning includes scrubbing, scraping, brushing, and ultrasonic procedures. Scrubbing with a bristle brush and mild abrasive is the most popular of these methods. The others are used in cases of heavy corrosion as a first step in removing heavily encrusted corrosion products prior to scrubbing. Care should be taken to avoid removing sound metal.

7.6.2 Chemical cleaning implies the removal of material from the surface of the coupon by dissolution in an appropriate solvent. Solvents such as acetone, dichloromethane, and alcohol are used to remove oil, grease, or resinous materials and are used prior to immersion to remove the products of corrosion. Solutions suitable for removing corrosion from the steel coupon are:

Solution	Soaking Time	Temperature
20 % NaOH + 200 g/L zinc dust	5 min	Boiling
or		

Conc. HC l + 50 g/L $SnC1_2$ + 20 g/L $SbC1_3$	Until clean	Cold

7.6.3 Electrolytic cleaning should be preceded by scrubbing to remove loosely adhering corrosion products. One method of electrolytic cleaning that can be employed uses:

Solution:	50 g/L H_2S0_4
Anode:	Carbon or lead
Cathode:	Steel coupon
Cathode current density:	20 amp/cm^2 (129 amp/in.^{2})
Inhibitor:	2 cc organic inhibitor/liter
Temperature:	74 degrees C (165 degrees F)
Exposure Period:	3 min.

<u>NOTE</u>: Precautions must be taken to ensure good electrical contact with the coupon to avoid contamination of the cleaning solution with easily reducible metal ions and to ensure that inhibitor decomposition has not occurred. Instead of a proprietary inhibitor, -0.5 g/L of either diorthotolyl thiourea of quinolin ethiodide can be used.

7.7 Whatever treatment is employed to clean the coupons, its effect in removing sound metal should be determined by using a blank (i.e., a coupon that has not been exposed to the waste). The blank should be cleaned along with the test coupon and its waste loss subtracted from that calculated for the test coupons.

7.8 After corroded specimens have been cleaned and dried, they are reweighted. The weight loss is employed as the principal measure of corrosion. Use of weight loss as a measure of corrosion requires making the assumption that all weight loss has been due to generalized corrosion and not localized pitting. In order to determine the corrosion rate for the purpose of this regulation, the following formula is used:

$$\text{Corrosion Rate (mmpy)} = \frac{\text{weight loss x 11.145}}{\text{area x time}}$$

where: weight loss is in milligrams,
area in square centimeters,
time in hours, and
corrosion rate in millimeters per year (mmpy).

8.0 QUALITY CONTROL

8.1 All quality control data should be filed and available for auditing.

8.2 Duplicate samples should be analyzed on a routine basis.

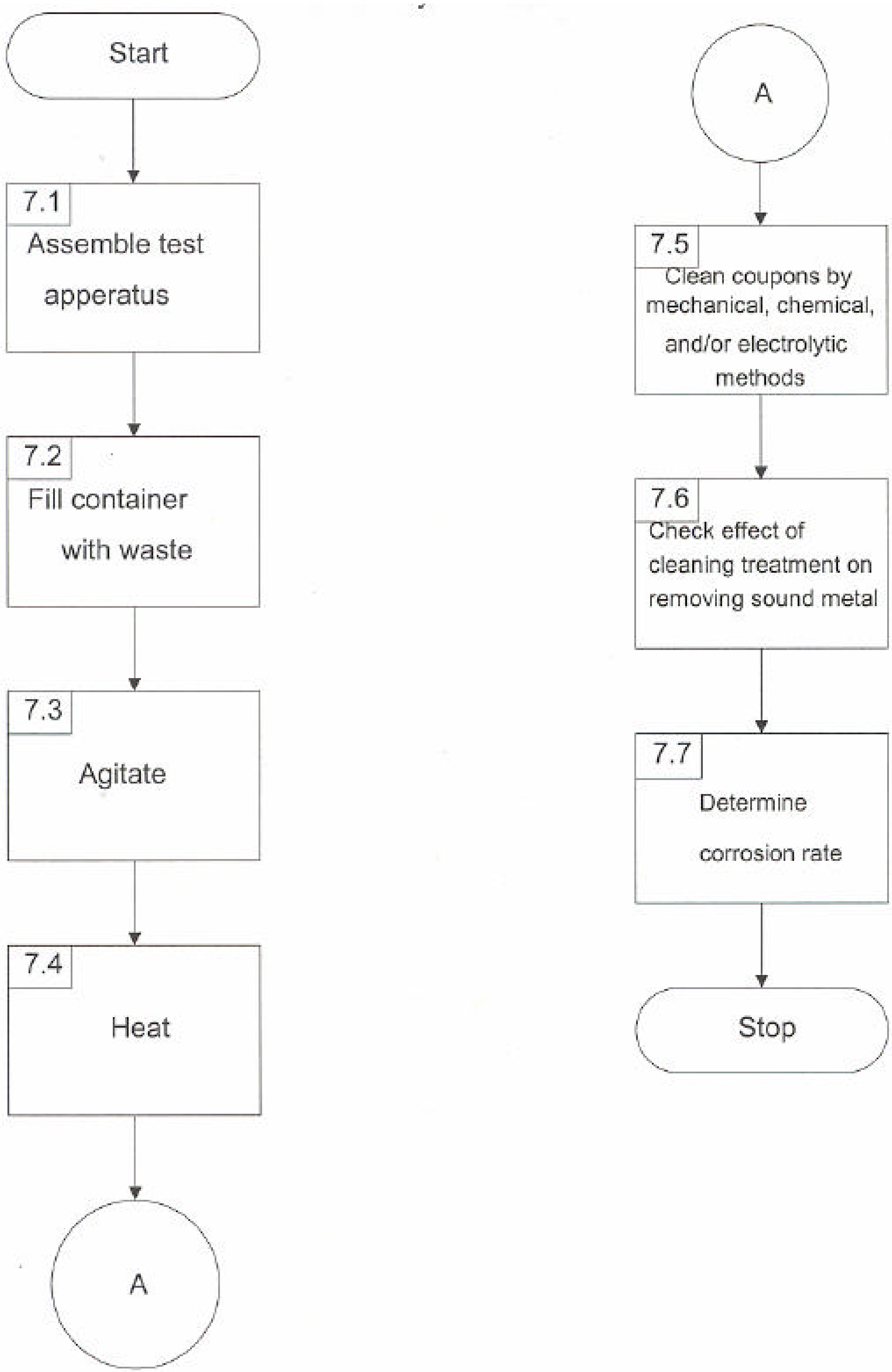
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. National Association of Corrosion Engineers, "Laboratory Corrosion Testing of Metals for the Process Industries," NACE Standard TM-01-69 (1972 Revision), NACE, 3400 West Loop South, Houston, TX 77027.

Method 1110
Corrosivity Toward Steel



3. D.1 METHOD 7.3.3.2

TEST METHOD TO DETERMINE HYDROGEN CYANIDE RELEASED FROM WASTES 1

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to all wastes, with the condition that wastes that are combined with acids do not form explosive mixtures.

1.2 This method provides a way to determine the specific rate of release of hydrocyanic acid upon contact with an aqueous acid.

1.3 This test measures only the hydrocyanic acid evolved at the test conditions. It is not intended to measure forms of cyanide other than those that are evolvable under the test conditions.

2.0 SUMMARY OF METHOD

2.1 An aliquot of acid is added to a fixed weight of waste in a closed system. The generated gas is swept into a scrubber. The analyte is quantitated. The procedure for quantitating the cyanide is Method 9014.

3.0 INTERFERENCES

3.1 Interferences are undetermined.

4.0 APPARATUS AND MATERIALS (See Figure 1)

4.1 Round-bottom flask - 500-mL, three-neck, with 24/40 ground-glass joints.

4.2 Gas scrubber - 50 mL calibrated scrubber

4.3 Stirring apparatus - To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination or an overhead motor-driven propeller stirrer.

4.4 Addition funnel - With pressure-equalizing tube and 24/40 ground-glass joint and Teflon sleeve. '

4.5 Flexible tubing - For connection from nitrogen supply to apparatus.

4.6 Water-pumped or oil-pumped nitrogen gas - With two-stage regulator.

4.7 Rotometer - For monitoring nitrogen gas flow rate.

4.8 Analytical balance - capable of weighing to 0.001 g.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sulfuric acid (O.O1N), HZS04. Add 2.8 mL concentrated H2S04to organic-free reagent water and dilute to 1 L. Withdraw 100 mL of this solution and dilute to 1 L to make the O.O1N HZS04;

5.4 Cyanide reference solution, (1000 mg/L). Dissolve approximately 2.5 g of KOH and 2.51 g of KCN in 1 liter of organic-free reagent water. Standardize with 0.0192N AgN03' Cyanide concentration in this solution should be 1 mg/mL.

5.5 Sodium hydroxide solution (1.25, NaOH. Dissolve 50 g of NaOH in reagent water and dilute to 1 liter with organic-free reagent water.

5.6 Sodium hydroxide solution (0.25N,, NaOH. Dilute 200 mL of 1.25N sodium hydroxide solution (Step 5.5) to 1 liter with organic-free reagent water.

5.7 Silver nitrate solution (0.0192N,. Prepare by crushing approximately 5 g of AgN03 crystals and drying to constant weight at 40°C. Weigh 3.265 g of dried AgN031. dissolve in organic-free reagent water, and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Samples containing, or suspected of containing, sulfide or a combination of sulfide and cyanide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should commence as soon as possible, and samples should be kept in a cool, dark place until analysis begins.

6.2 It is suggested that samples of cyanide wastes be tested as quickly as possible. Although they can be preserved by adjusting the sample pH to 12 with strong base, this will cause dilution of the sample, increase the ionic strength, and, possibly, change other physical or chemical characteristics of the waste which may affect the rate of release of the hydrocyanic acid. Storage of samples should be under refrigeration and in the dark.

6.3 Testing should be performed in a ventilated hood.

7.0 PROCEDURE

7.1 Add 50 mL of 0.25N NaOH solution (Step 5.6) to a calibrated scrubber and dilute with organic-free reagent water to obtain an adequate depth of liquid.

7.2 Close the system and adjust the flow rate of nitrogen, using the rotometer. Flow should be 60 mL/min.

7.3 Add 10 g of the waste to be tested to the system.

7.4 With the nitrogen flowing, add enough sulfuric acid to fill the flask half full. Start the 30 minute test period.

7.5 Begin stirring while the acid is entering the round-bottom flask. The stirring speed must remain constant throughout the test.

NOTE: The stirring should not be fast enough to create a vortex.

7.6 After 30 minutes, close off the nitrogen and disconnect the scrubber. Determine the amount of cyanide in the scrubber by Method 9014.

NOTE: Delete the "C" and "D" terms from the spectrophotometric procedure calculation and the "E" and "F" terms from the titration procedure calculation in Method 9014. These terms are not necessary for the reactivity determination because the terms determine the amount of cyanide in the entire sample, rather than only in the aliquot taken for analysis.

8.0 CALCULATIONS

8.1 Determine the specific rate of release of HCN, using the following parameters:

X = Concentration of HCN in diluted scrubber solution (mg/L)
(This is obtained from Method 9014.)

L = Volume of solution in scrubber (L)

W = Weight of waste used (kg)

S = Time of measurement (sec.) = Time N_2 stopped - Time N_2 started

$$R = \text{specific rate of release (mg/kg/sec.)} = \frac{X ? L}{W ? S}$$

Total releasable HCN (mg/kg) = R x S

9.0 METHOD PERFORMANCE

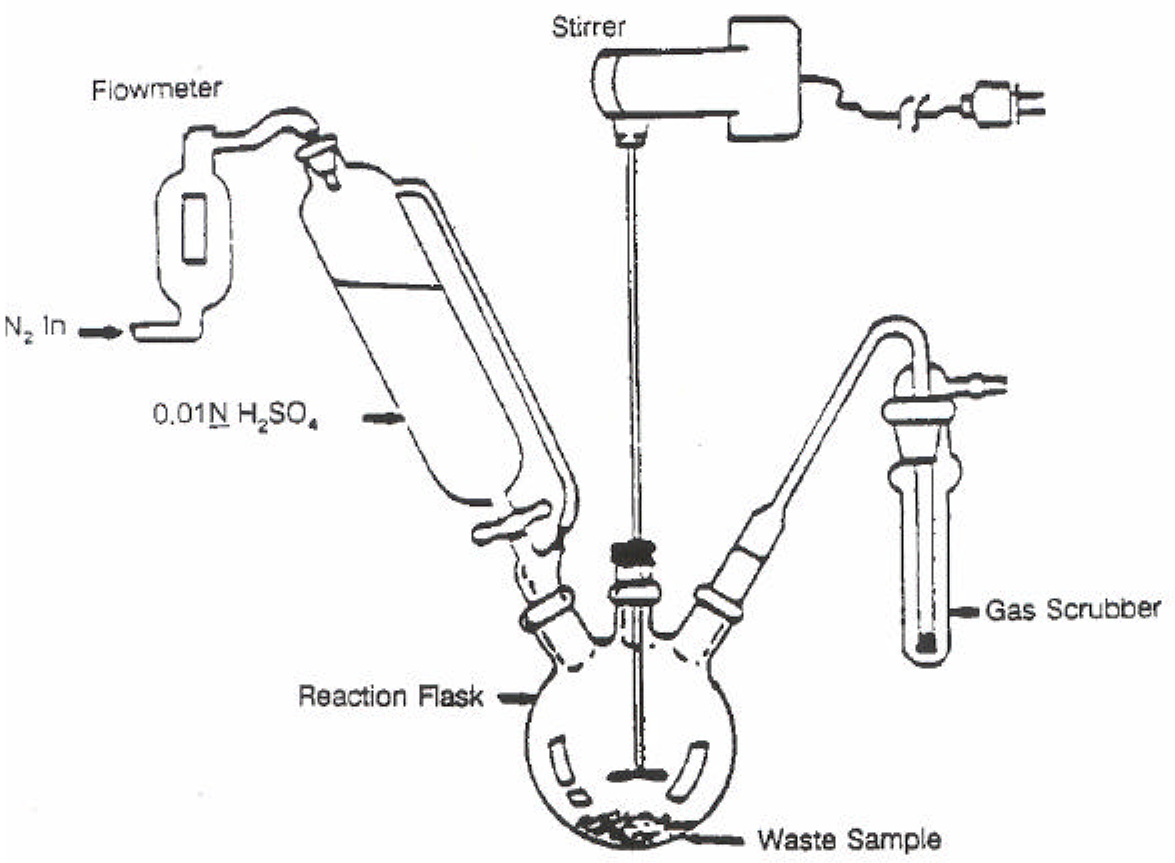
9.1 The operation of the system can be checked and verified using the cyanide reference solution (Step 5.4). Perform the procedure using the reference solution as a sample and determine the percent recovery. Evaluate the standard recovery based on historical laboratory data, as stated in Chapter One.

10.0 REFERENCES

10.1 No references are available at this time.

FIGURE 1.

APPARATUS TO DETERMINE HYDROGEN CYANIDE RELEASED FROM WASTES



3.D.2 METHOD 7.3.4.2

TEST METHOD TO DETERMINE HYDROGEN SULFIDE RELEASED FROM WASTES

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to all wastes, with the condition that wastes that are combined with acids do not form explosive mixtures.

1.2 This method provides a way to determine the specific rate of release of hydrogen sulfide upon contact with an aqueous acid.

1.3 This procedure releases only the hydrogen sulfide evolved at the test conditions. It is not intended to measure forms of sulfide other than those that are evolvable under the test conditions.

2.0 SUMMARY OF METHOD

2.1 An aliquot of acid is added to a fixed weight of waste in a closed system. The generated gas is swept into a scrubber. The analyte is quantified. The procedure for quantifying the sulfide is given in Method 9034.

3 .0 INTERFERENCES

3.1 Interferences are undetermined.

4.0 APPARATUS AND MATERIALS (See Figure 2)

4.1 Round-bottom flask - 500-mL, three-neck, with 24/40 ground-glass joints.

4.2 Gas scrubber - 50 mL calibrated scrubber.

4.3 Stirring apparatus - To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination or an overhead motor-driven propeller stirrer.

4.4 Addition funnel - With pressure-equalizing tube and 24/40 ground-glass joint and Teflon sleeve.

4.5 Flexible tubing - For connection from nitrogen supply to apparatus.

4.6 Water-pumped or oil-pumped nitrogen gas - With two-stage regulator.

4.7 Rotometer - For monitoring nitrogen gas flow rate.

4.8 Analytical balance - capable of weighing to 0.001 g.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sulfuric acid (O.O1N), H_2S0_4. Add 2.8 mL concentrated H_2S0_4 to organic-free reagent water and dilute to 1 L. Withdraw 100 mL of this solution and dilute to 1 L to make the O.O1N H_2S0_4.

5.4 Sulfide reference solution - Dissolve 4.02 g of $Na_2S \cdot 9H_20$ in 1.0 L of organic-free reagent water. This solution contains 570 mg/L hydrogen sulfide. Dilute this stock solution to cover the analytical range required (100-570 mg/L).

5.5 Sodium hydroxide solution (0.25N), NaOH. Dissolve 50 g of NaOH in organic-free reagent water and dilute to 1 L with organic-free reagent water.

5.6 Sodium hydroxide solution (0.25N), NaOH. Dilute 200 ml, of 1.25N sodium hydroxide solution (Step 5.5) to 1 L with organic-free reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Samples containing, or suspected of containing, sulfide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should commence as soon as possible, and samples should be kept in a cool, dark place until analysis begins.

6.2 It is suggested that samples of sulfide wastes be tested as quickly as possible. Although they can be preserved by adjusting the sample pH to 12 with strong base and adding zinc acetate to the sample, these will cause dilution of the sample, increase the ionic strength, and, possibly, change other physical or chemical characteristics of the waste which may affect the rate of release of the hydrogen sulfide. Storage of samples should be under refrigeration and in the dark. '"

6.3 Testing should be performed in a ventilated hood.

7.0 PROCEDURE

7.1 Add 50 mL of 0.25N NaOH solution to a calibrated scrubber and dilute with organic-free reagent water to obtain an adequate depth of liquid.

7.2 Assemble the system and adjust the flow rate of nitrogen, using the rotometer. Flow should be 60 mL/min.

7.3 Add 10 g of the waste to be tested to the system.

7.4 With the nitrogen flowing, add enough sulfuric acid to fill the flask half full, while starting the 30 minute test period.

7.5 Begin stirring while the acid is entering the round-bottom flask. The stirring speed must remain constant throughout the test.

NOTE: The stirring should not be fast enough to create a vortex.

7.6 After 30 minutes, close off the nitrogen and disconnect the scrubber. Determine the amount of sulfide in the scrubber by Method 9034.

7.7 Substitute the following for Step p7.3.2 in Method 9034: The trapping solution must be brought to a pH of 2 before proceeding. Titrate a small aliquot of the trapping solution to a pH 2 end point with 6N HCI and calculate the amount of HCI needed to acidify the entire scrubber solution. Combine the small acidified aliquot with the remainder of the acidified scrubber solution.

8.0 CALCULATIONS

8.1 Determine the specific rate of release of HZS, using the following parameters:

X = Concentration of H2S in scrubber (mg/L). (This is obtained from Method 9034.)

L = Volume of solution in scrubber (L)

W = Weight of waste used (kg)

S = time of experiment (sec.) = Time NZ stopped - Time NZ started

R = specific rate of release (mg/kg/sec.) = $\frac{X ? L}{W ? S}$

Total releasable H_2S (mg/kg) = R x S

9.0 METHOD PERFORMANCE

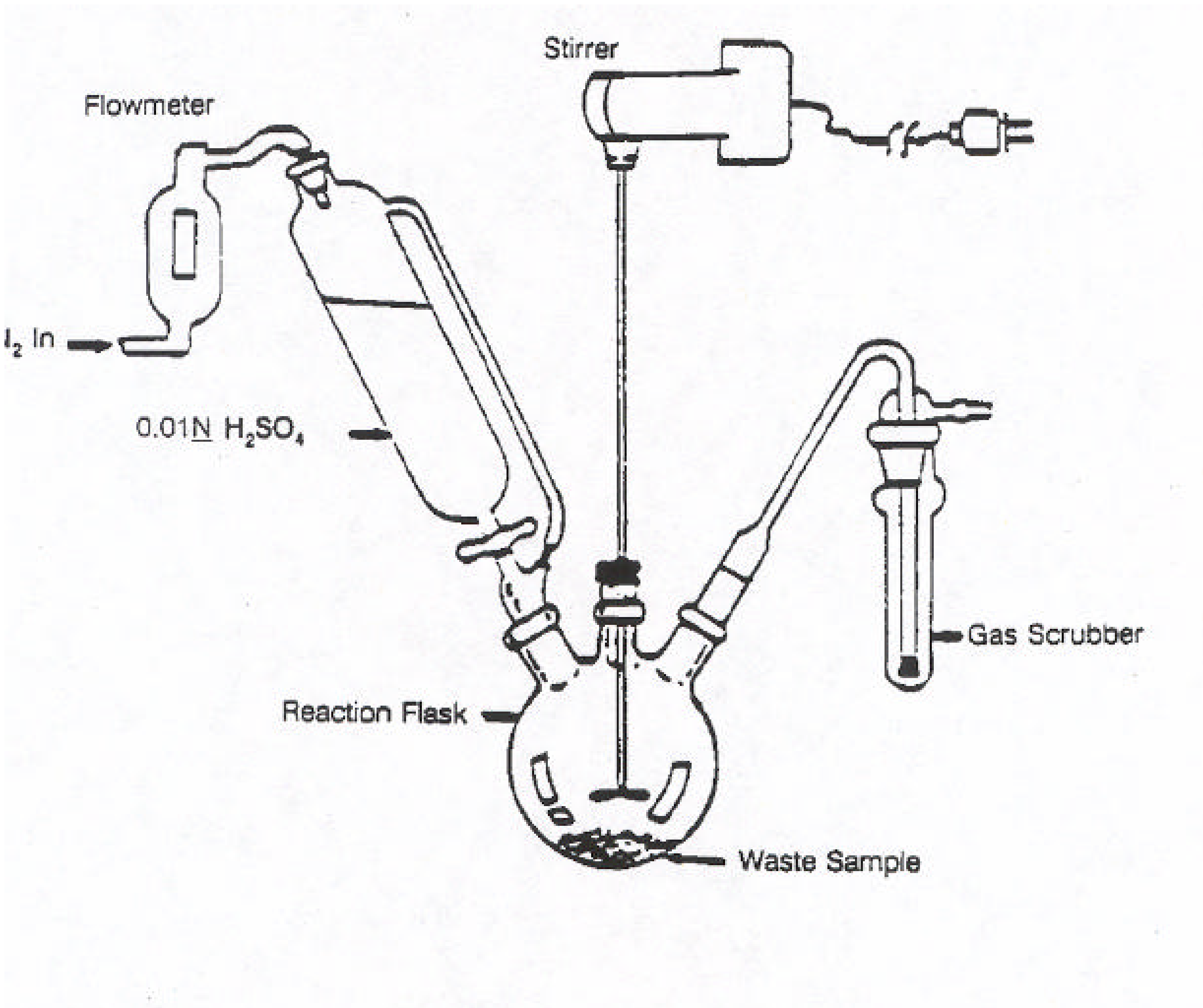
9.1 The operation of the system can be checked and verified using the sulfide reference solution (Step 5.4). Perform the procedure using the reference solution as a sample and determine the percent recovery. Evaluate the standard recovery based on historical laboratory data, as stated in Chapter One.

10.0 REFERENCES

10.1 No references are available at this time.

FIGURE 2.

APPARATUS TO DETERMINE HYDROGEN SULFIDE RELEASED FROM WASTES



3.D.3 METHOD 9014

TITRIMETRIC AND MANUAL SPECTROPHOTOMETRIC DETERMINATIVE METHODS FOR CYANIDE

1.0 SCOPE AND APPLICATION

1.1 This method can be used for measuring free (non-complexed) cyanide and hydrocyanic acid in drinking water, natural surface waters, domestic and industrial wastewater, and in soil extracts. This method may also be used as a determinative step for quantifying total and amenable cyanide in the alkaline distillates from Method 9010.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 0.1 mg/L (0.025 mg/250 mL of absorbing liquid):

1.3 The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

2.0 SUMMARY OF METHOD

2.1 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCI) by reaction of cyanide with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 578 nm for the complex formed with pyridine-barbituric acid reagent and CNCI. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.2 The titration measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure provided in Method 9010.

Refer to Method 9010 for a discussion of potential cyanide interferences.

4.0 APPARATUS AND MATERIALS

4.1 Spectrophotometer - Suitable for measurements at 578 nm with a 1.0 cm cell or larger.

4.2 Hot plate stirrer/hearing mantle.

4.3 pH meter.

4.4 Refrigerator.

4.5 5 ml, microburette.

4.6 Class A volumetric flasks - 1000, 250, and 100 mL.

4.7 Erlenmeyer flask - 500 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it , is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Reagents for spectrophotometric determination

5.3.1 Sodium hydroxide solution (0.25N), NaOH. Dissolve 10 g NaOH in 1 liter of water.

5.3.2 Sodium phosphate monobasic (1M), NaH_2P0_4? H_20. Dissolve 138 g of NaH_2P0_4?H_20 in 1 liter of water. Refrigerate this solution.

5.3.3 Chloramine-T solution (0.44%), $C_7H_7CINNaO_2S$. Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of water and refrigerate until ready to use.

5.3.4 Pyridine-Barbituric acid reagent, C_5H_5N ? $C_4H_4N_20_3$. Place 15 g of barbituric acid in a 250-ml, volumetric flask and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 ml, of pyridine and mix. Add 15 mL of concentrated hydrochloric acid (HCI), mix, and cool to room temperature. Dilute to 250 mL with water. This reagent is stable for approximately six months if stored in a cool, dark place.

5.3.5 Stock potassium cyanide solution (1 mL = 1000 µg CN), KCN. Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of water. Standardize with 0.0192N silver nitrate, AgN03. Dilute to appropriate concentration to achieve 1 mL = 1000 µg of CN.

NOTE: Detailed procedure for AgN03 standardization is described in "Standard Methods for the Examination of Water and Wastewater," 18th Edition, (1992), Methods 4500-CN D.

5.3.6 Intermediate standard potassium cyanide solution, (1 mL = 100 µg CN), KCN. Dilute 100 mL of stock potassium cyanide solution (1 mL = 1000 µg CN) to 1000 mL with water.

5.3.7 Working standard potassium cyanide solution, (1 mL = 10 pg CN), KCN. Prepare fresh daily by diluting 100 ml, of intermediate standard potassium cyanide solution and 10 mL of 1N NaOH to 1 liter with water:

5.4 Reagents for titration procedure

5.4.1 Rhodanine indicator - Dissolve 20 mg of p-dimethylamino-benzal-rhodanine, $C_{12}H_{12}N_2OS_2$, in 100 mL of acetone.

5.4.2 Standard silver nitrate solution (0.0192N), AgN03. Prepare by crushing approximately 5 g $AgN0_3$ and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgN0_3$. Dissolve in 1 liter of water.

NOTE: Detailed procedure for $AgN0_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater," 18th Edition, (1992), Method 4500-CN D.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 9010 for guidance on sample collection, preservation, and handling.

6.2 Distillates that are not analyzed immediately should be stored in tightly sealed flasks at 4°C.

7.0 PROCEDURE

7.1 If the manual spectrophotometric determination will be performed, proceed to Section 7.2. If the titration procedure will be performed, proceed to Section 7.6.

7.2 Manual spectrophotometric determination

7.2.1 Pipet 50 mL of sample or 50 mL of the scrubber solution obtained from the distillation procedure in Method 9010 into a 100-mL volumetric flask. If the sample is later found to be beyond the linear range of the colorimetric determination and redistillation of a smaller sample is not feasible, a smaller aliquot may be taken. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution.

NOTE: Temperature of reagents and spiking solution can affect the response factor of the colorimetric determination. The reagents stored in the refrigerator should be warmed to ambient temperature before use. Samples should not be left in a warm instrument to develop color, but instead they should be aliquoted to a cuvette immediately prior to reading the absorbance.

7.2.2 Add 15 mL of 1M sodium phosphate solution and mix. Add 2 mL of chloramine-T and mix. Some distillates may contain compounds that have chlorine demand. One minute after the addition of chloramine-T, test for excess chlorine with KI-starch paper. If the test is negative, add 0.5 mL chloramine-T. After one minute recheck with KI-starch paper. Continue to add chloramine-T in 0.5 mL increments until an excess is maintained. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution and mix.

7.2.3 Dilute to 100 mL with water and mix again. Allow 8 minutes for color development and then read the absorbance at 578 nm in a 1-cm cell within 15 minutes. The sodium hydroxide concentration will be 0.125N.

7.3 Standard curve for samples without sulfide

7.3.1 Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25N sodium hydroxide and dilute to 250 mL with water. Prepare using the following table. The sodium hydroxide concentration will be 0.25N.

mL of Working Standard Solution (1 mL = 10 µg CN)	Concentration (µg CN/L)
0	Blank
1.0	40
2.0	80
5.0	200
10.0	400
15.0	600
20.0	800

7.3.2 After the standard solutions have been prepared according to the table above, pipet 50 mL of each standard solution into a 100-mL volumetric flask and

Chemical Testing Methods for Designating Dangerous Waste

proceed to Sections 7.2.2 and 7.2.3 to obtain absorbance values for the standard curve. ', The final concentrations for the standard curve will be one half of the amounts in the above table (final concentrations ranging from 20 to 400 µg/L.

7.3.3 Prepare a standard curve ranging from 20 to 400 µg/L by plotting absorbance of standard versus the cyanide concentration.

7.4 Standard curve for samples with sulfide

7.4.1 It is imperative that all standards be distilled in the same manner as the' samples using the method of standard additions. Standards distilled by this method will give a linear curve, at low concentrations, but as the concentration increases, the recovery decreases. It is recommended that at least five standards be distilled.

7.4.2 Prepare a series of standards similar in concentration to those mentioned ' in Section 7.3.1 and analyze as in Section 7.2. Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration.

7.5 Calculation - If the spectophotometric procedure is used, calculate the cyanide, in µg/L, in the original sample as follows.

$$CN\ (\mu g/L) = \frac{AxBxC}{DxE}$$

where:

Å = µg/L CN read from standard curve.
B = ml, of sample after preparation of colorimetric analysis (100 mL recommended).
C = mL of sample after distillation (250 ml, recommended).
D = mL of original sample for distillation (500 mL recommended.)
E = mL used for colorimetric analysis (50 ml, recommended).

7.6 Titration Procedure

7.6.1 Transfer the gas scrubber solution or a suitable aliquot from the 250-mL volumetric flask to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator.

7.6.2 Titrate with standard 0.0192N silver nitrate to the first change in color from yellow to brownish-pink. The titration must be performed slowly with constant stirring. Titrate a water blank using the same amount of sodium hydroxide and indicator as in the sample. The analyst should be familiar with the endpoint of the titration and the amount of indicator to be used before actually titrating the samples. A 5-ml, buret may be conveniently used to obtain a precise titration:

NOTE: The titration is based on the following reaction:

$Ag^{+} + 2CN$? $\{Ag(CN)_2]$

When all of the cyanide has complexed and more silver nitrate is added, the excess silver combines with the rhodanine indicator to turn the solution yellow and then brownish-pink.

7.6.3 Calculation - If the titrimetric procedure is used, calculate concentration of CN- in µg/L in the original sample as follows:

$$CN\text{-}(\mu g/L) = \frac{(A - B)}{C} \times D \times \frac{E}{F} \times \frac{2\ mole\ CN^{-}}{1\ eq.\ 4gNO_3} \times \frac{26.02\ g\ CN^{-}}{1\ mole\ CN^{-}} \times \frac{1 \times 10^{6}\ \mu g}{1\ g}$$

where:

A = ml, of $AgN0^{3}$ for titration of sample.
B = ml, of $AgN0_3$ for titration of blank.
C = ml, of sample titrated (250 recommended).
D =actual normality of $AgN0_3$ (0.0192N recommended).
E = mL of sample after distillation (250 recommended).
F = mL of original sample before distillation (500 recommended).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Refer to the quality control section of Method 9010A for the method requirements for blanks, matrix duplicates, and matrix spikes. Each QC sample must be processed through the reflux-distillation steps contained in Method 9010 prior to analysis by this method.

8.3 Analyze check standards with every analytical batch of samples. If the standards are not within 15% of the expected value, then the samples must be reanalyzed.

8.4 Analyze one replicate sample for every 20 samples. The CV of the replicates should be 20% or less. If this criterion is not met, the samples should be reanalyzed.

8.5 Analyze one matrix spiked sample every 20 samples to check the efficiency of sample distillation procedure and to monitor potential matrix interference.

8.6 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

9.0 METHOD PERFORMANCE

9.1 The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

9.2 EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.06 to 0.62 mg/L CN-, the standard deviations for precision were ± 0.005 to t 0.094, respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0. 62 mg/L CN-, recoveries (accuracy) were 85 % and 102 % ,respectively.

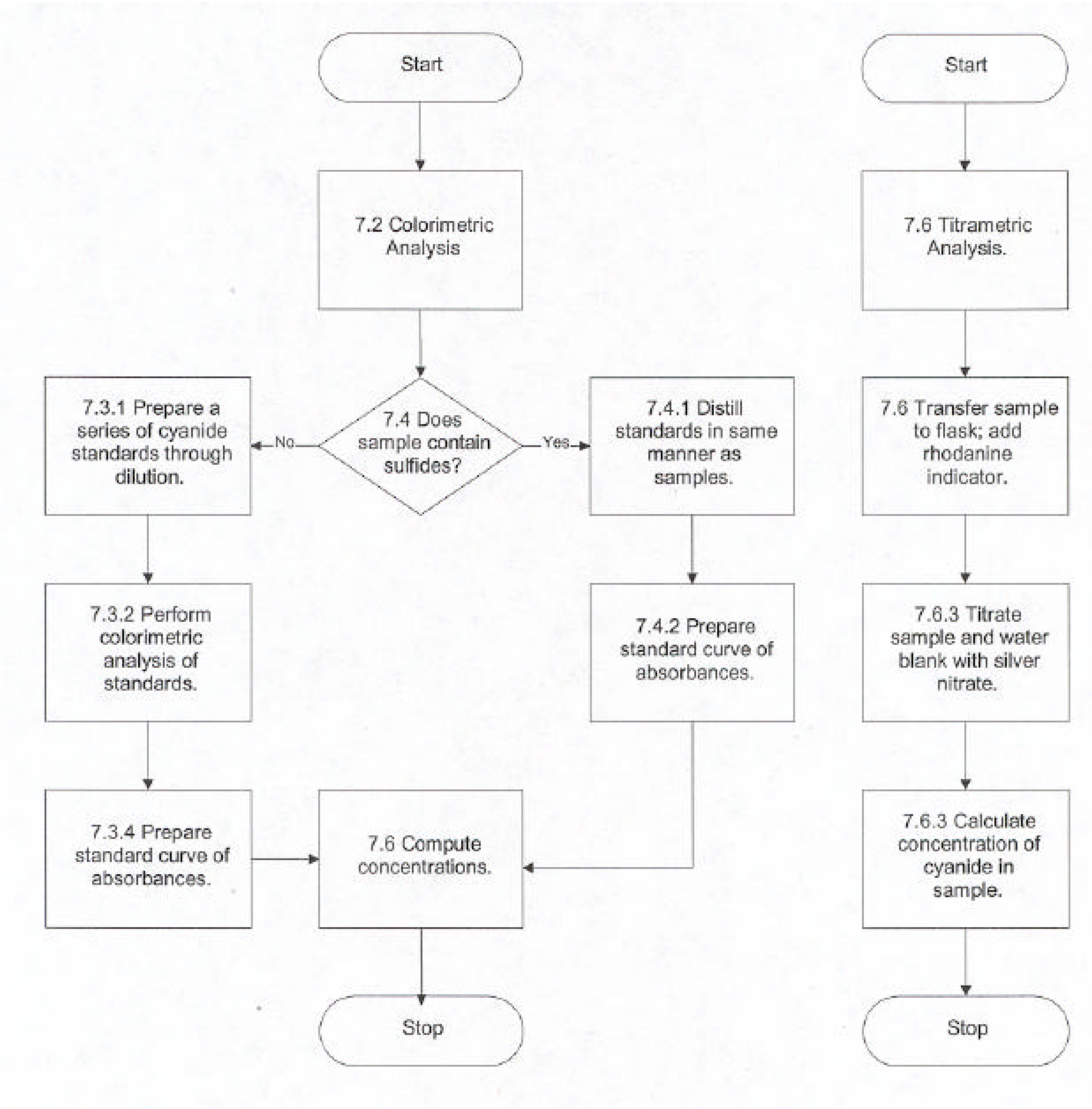
9.3 In two additional studies using surface water, ground water, and landfill leachate samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94 % and 98 .9 % for total cyanide, and 86.7 % and 97.4 % for amenable cyanide.

10.0 REFERENCES

10.1 Refer to Method 9010 for references on total and amenable cyanide.

METHOD 9014

TITRIMETRIC AND MANUAL SPECTROPHOTOMETRIC DETERMINATIVE METHODS FOR CYANIDE



3.D.4 METHOD 9034

TITRIMETRIC PROCEDURE FOR ACID-SOLUBLE AND ACID INSOLUBLE SULFIDES

1.0 SCOPE AND APPLICATION

1.1 This procedure may be used as a determinative step for acid-soluble and acid-insoluble sulfides following distillation of the sample by SW-846 Method 9030.

1.2 Method 9034 is suitable for measuring sulfide concentrations in samples which contain 0.2 mg/kg to 50 mg/kg of sulfide.

2.0 SUMMARY OF METHOD

Sulfide is extracted from the sample by a preliminary distillation procedure (See Method 9030) and precipitated in a zinc acetate scrubber as zinc sulfide. The sulfide is oxidized to sulfur by adding a known excess amount of iodine. The excess iodine is determined by titration with a standard solution of phenyl arsine oxide (PAO) or sodium thiosulfate until the blue iodine starch complex disappears. As the use of standard sulfide solutions is not possible because of oxidative degradation, quantitation is based on the PAO or sodium thiosulfate.

3 .0 INTERFERENCES

3.1 The iodometric method suffers interference from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds.

3.2 Refer to Method 9030 for a discussion of other sulfide interferences.

4.0 APPARATUS AND MATERIALS

4.1 500 mL flasks.

4.2 Hot plate stirrer.

4.3 25 mL buret.

4.4 Volumetric pipets.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as ',, defined in Chapter One.

5.3 Starch solution - Use either an aqueous solution or soluble starch powder mixtures. Prepare an aqueous solution as follows. Dissolve 2 g soluble starch and 2 g salicylic acid, C711603, as a preservative, in 100 ml, hot reagent water.

5.4 Iodine solution (approximately 0.025N)

5.5 Dissolve 25 g potassium iodide, KI, in 700 mL of reagent water in a 1-liter volumetric flask. Add 3.2 g iodine, 12. Allow to dissolve. Add the type and amount of acid specified in Section 7.3.2. Dilute to 1 liter and standardize as follows.

5.6 Dissolve approximately 2 g KI in 150 nil, of reagent water. Add exactly 20 mL of the iodine solution (Section 5.4) to be titrated and dilute to 300 ml, with reagent water.

5.6.1 Titrate with 0.025N standardized phenylarsine oxide or 0.025N sodium thiosulfate until the amber color fades to yellow. Add starch indicator solution. Continue titration drop by drop until the blue color disappears.

5.6.2 Run in replicate

5.6.3 Calculate the normality as follows.

$$\text{Normality } (I_2) = \frac{\textit{mL of titrant x normality of titrant}}{\textit{sample size in mL}}$$

5.7 Sodium sulfide nonanhydrate, Na_2S ? $9H_20$. For the preparation of standard solutions to be used for calibration curves. Standards must be prepared at pH > 9 and < 11. Protect standard from exposure to oxygen by preparing it without headspace. These standards are unstable and should be prepared daily.

5.8 Titrant.

5.8.1 Standard phenylarsine oxide solution (PAO) (0.025N), C6HSAs0. This solution is commercially available.

CAUTION: PAO is toxic.

5.8.2 Standard sodium thiosulfate solution (0.025N), $Na_2S_20_3$? $5H_20$. Dissolve 6.205 ± 0.005 $Na_2S_20_3$? $5H_20$ in 500 ml, reagent water. Add 9 ml, 1N NaOH and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 9030 for a discussion of sample collection, preservation, and handling.

6.2 Distillates that are not analyzed immediately should be stored in a sealed flask at ' 4°C.

7.0 PROCEDURE

7.1 The following iodometric titration procedure is used to quantify the sulfide concentration in the distillate generated by Method 9030.

7.3.1 Pipet a known amount of standardized 0.025N iodine solution (see Section 5.4) in a 500-mL flask, adding an amount in excess of that needed to oxidize the sulfide. Add enough reagent water to bring the volume to 100 mL. The volume of standardized iodine solution should be about 65 mL for samples with 50 mg of sulfide.

7.3.2 If the distillation for acid-soluble sulfide is being used, add 2 mL of 6N HCI. If the distillation for acid-insoluble sulfides is performed, 10 mL of 6N HCI should be added to the iodine.

7.3.3 Pipet the gas scrubbing solutions obtained in Method 9030 to the flask, keeping the end of the pipet below the surface of the iodine solution. If at any point in transferring the zinc acetate solution or rinsing the bottles, the amber color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Section 7.3.1 for calculations. Record the total volume of standardized 0.025N iodine solution used.

7.3.4 Prepare a rinse solution of a known amount of standardized 0.025N iodine solution, 1 ml, of 6N HCI, and reagent water to rinse the remaining white precipitate (zinc sulfide) from the gas scrubbing bottles into the flask. There should be no visible traces of precipitate after rinsing.

7.3.5 Rinse any remaining traces of iodine from the gas scrubbing bottles with reagent water, and transfer the rinsate to the flask.

7.3.6 Titrate the solution in the flask with standard 0.025N phenylarsine oxide or 0.025N sodium thiosulfate solution until the amber color fades to yellow: Add enough starch indicator for the solution to turn dark blue and titrate until the blue disappears. Record the volume of titrant used.

7.3.7 Calculate the concentration of sulfide using the following equation:

$$\underline{(\text{mL } 12 \text{ x N } 12) - (\text{mL titrant x N titrant})} \text{ x} \left[\frac{32.06g}{2\ eq.}\right] = \text{sulfide (mg/kg or mg/L}$$

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by or under supervision of experienced analysts. Refer to Method 9030 for additional quality control guidelines.

8.2 A reagent blank should be analyzed once in twenty analyses or per analytical batch, whichever is more frequent.

8.3 Check standards are prepared from water and a known amount of sodium sulfide. A check standard should be run with each analytical batch of samples, or once in twenty samples. Acceptable recovery will depend on the level and matrix.

8.4 A matrix spiked sample should be analyzed for each analytical batch or twenty samples, whichever is more frequent, to determine matrix effects. If recovery is low, acid-insoluble sulfides are indicated. A matrix spiked sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Refer to Method 9030 for data on the precision and accuracy of this method.

10.0 REFERENCES

1. <u>Test Methods for Evaluating Solid Waste, Physical/Chemical Methods</u>, SW-846, 2nd ed.; U.S. Environmental Protection Agency. Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC.

2. <u>Methods for Chemical Analysis of Water and Wastes</u>; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1979; EPA-600/4-79-020.

3. <u>CRC Handbook of Chemistry and Physics</u>, 66th ed.; West, R., Ed.; CRC: Boca Raton, FL, 1985.

4. Standard Methods for the Examination of Water and Wastewater, 16th ed.; Greenberg, ', A.E.; Trussell, R.R.; Clesceri, L.S., Eds.; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, DC, 1985; Methods 427, 427A, 427B, and 427D.

5. Andreae, M.O.; Banard, W.R. Anal. Chem. 1983, 55, 608-612.

6. Barclay, H. Add: Instrum. 1980, 35(2), 59-61.

7. Bateson, S.W.; Moody, G.J.; Thomas, J.P.R. Analyst 1986, 111, 3-9.

8. Berthage, P.O. Anal. Chim. Acta 1954, 10 310-311.

9. Craig, P.J.; Moreton, P.A. Environ. Technol. Lett. 1982, 3, 511-520.

10. Franklin, G.O.; Fitchett, A.W. Pulp & Paper Canada 1982, 83(10), 40-44.

11. Fuller, W. In Cyanide in the Environment; Van Zyl, D., Ed.; Proceedings of Symposium; December, 1984.

12. Gottfried, G.J. "Precision, Accuracy, and MDL Statements for EPA Methods 9010, 9030, 9060, 7520, 7521, 7550, 7551, 7910, and 7911"; final report to the U.S. Environmental Protection Agency (EMSL-CI); Biopheric.

13. Kilroy, W.P. Talanta 1983, 30(6), 419-422.

14. Kurtenacher, V.A.; Wallak, R. Z. Anor . U. Ally. Chem. 1927, 161 202-209.

15. Landers, D.H.; David, M.B.; Mitchell, M.J. Int. J. Anal. Chem 1983, 14, 245-256.

16. Opekar, F.; Brukenstein, S. Anal. Chem. 1984, 56, 1206-1209.

17. Ricklin, R.D.; Johnson, E.L. Anal. Chem. 1983, 55, 4.

18. Rohrbough, W. G. ; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

19. Snedecor, G.W.; Ghran, W.G. Statistical Methods; Iowa State University: Ames, IA, 1980.

20. Umana, M.; Beach, J.; Sheldon, L. "Revisions to Method 9010"; final report to the U.S. Environmental Protection Agency on Contract No. 68-01-7266; Research Triangle Institute: Research Triangle Park, NC, 1986; Work Assignment No. 1.

21. Umana, M.; Sheldon, L. "Interim Report: Literature Review"; interim report to the U.S. Environmental Protection Agency in Contract No. 68-01-7266; Research Triangle Institute: Research Triangle Park, NC, 1986; Work Assignment No. 3.

22. Wang, W.; Barcelona, M.J. Environ. Inter. 1983, 9, 129-133.

23. Wronski, M. Talanta 1981, 28, 173-176.

24. Application Note 156; Princeton Applied Research Corp.: Princeton, NJ.

25. Guidelines for Assessing and Reporting Data Quality for Environmental Measurements; U.S. Environmental Protection Agency. Office of Research and Development. U.S. Government Printing Office: Washington, DC, 1983.

26. Fed. Regist. 1980, 45(98), 33122.

27. The Analytical Chemistry of Sulfur and Its Compounds, Part I; Karchmer, J.H., Ed.; Wiley-Interscience: New York, 1970.

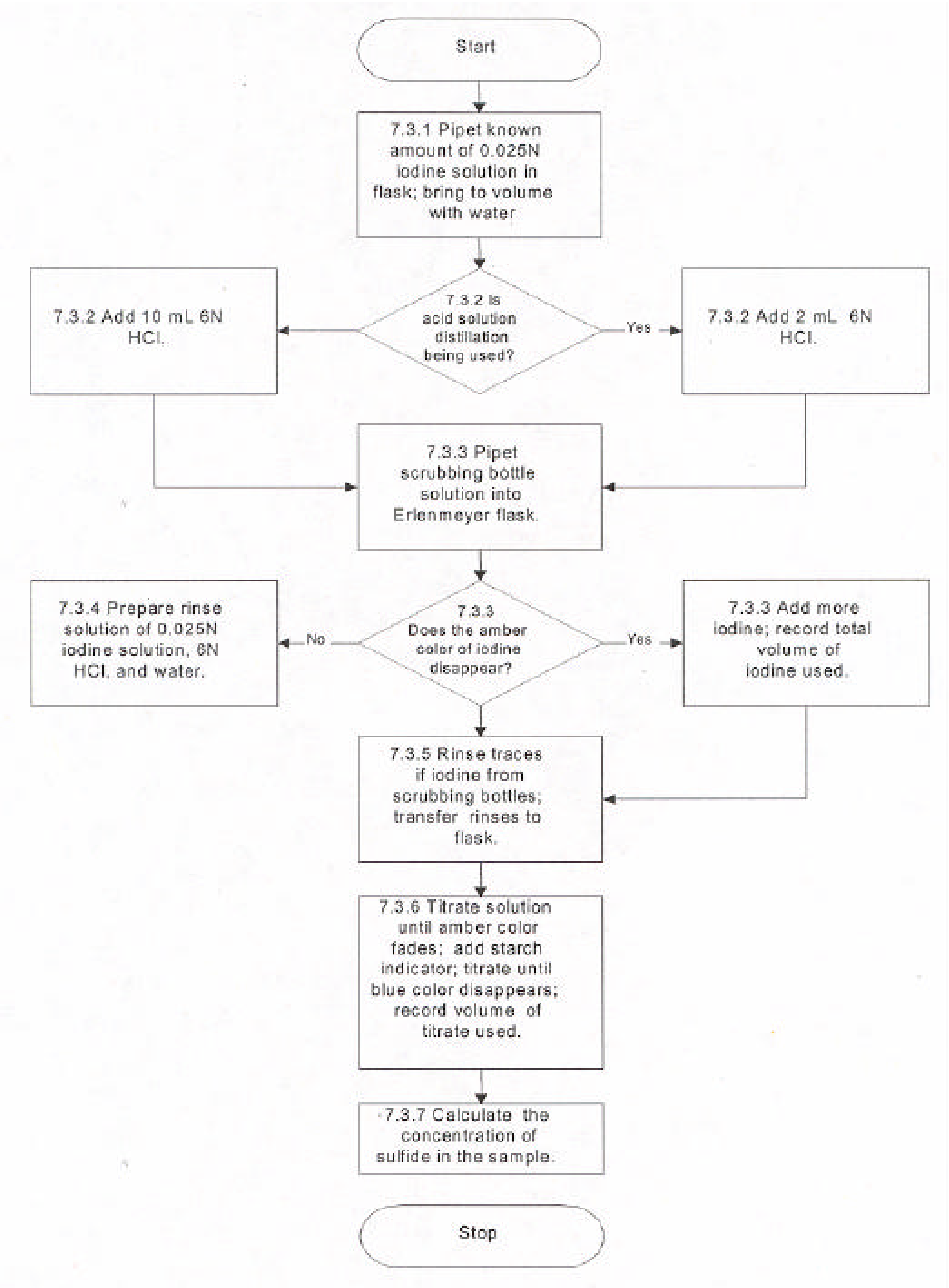
28. Methods for the Examination of Water and Associated Materials; Department of the Environment: England, 1983.

29. "Development and Evaluation of a Test Procedure for Reactivity Criteria for Hazardous Waste"; final report to the U.S. Environmental Protection Agency on Contract 68 03-2961; EAL: Richmond, CA.

30. Test Method to Determine Hydrogen Sulfide Released from Wastes; U.S. Environmental Protection Agency. Office of Solid Waste. Preliminary unpublished protocol, 1985.

31. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 9034
TITRIMETRIC PROCEDURE FOR ACID-SOLUBLE AND ACID INSOLUBLE SULFIDES



3. E.1 METHOD 1311

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

1.3 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.0 SUMMARY OF METHOD

2.1 For liquid wastes (i.e., those containing less than 0.5 percent dry solid material), the waste, after filtration through a 0.6 to 0.8 pm glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than or equal to 0.5 percent solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 pm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels

4.2.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of volatile analytes i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Section 4.3.1). The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[4] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to I, be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Section 7.3) refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is .measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

[4] VITON® is a trademark of Du Pont.

4.2.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Section 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Section 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in Section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

> NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Section 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (less thanl0percent) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4:

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern..

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 gm, or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with IN nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to ± 0.05 units at 25 degrees C.

4.6 ZHE Extract Collection Devices: TEDLAR®5 bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., less than 1 percent of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., greater than 1 percent of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100 percent solid) or has no significant phase (is 100 percent liquid), either the TEDLAR© bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.~., a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (see Section 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

5 TEDLAR® is a registered trademark of Du Pont.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.2.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.2.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 ± S degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.3 Hydrochloric acid (1N), HC I, made from ACS reagent grade.

5.4 Nitric acid (1N), $HN0_3$ made from ACS reagent grade.

5.5 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.6 Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade.

5.7 Extraction fluid.

5.7.1 Extraction fluid # 1: Add 5.7 mL glacial CH3CHZOOH to 500 mL of reagent water (See Section 5.2), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05. , 5.7.2 Extraction fluid # 2: Dilute 5.7 mL glacial CH3CHZOOH with reagent water (See Section 5.2) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 ± 0.05.

> NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.8 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction (see Section 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4 degrees C. Samples should be opened only immediately prior to extraction).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH less than 2, unless precipitation occurs (see Section 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 8.0 (QA requirements) for acceptable sample and extract holding times.

7.0 PROCEDURE

7.1 Preliminary Evaluations

Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids (Section 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Section 7.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (Section 7.1.4).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (Le., is 100 percent solids) proceed to Section 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered I followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 degrees C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

> NOTE: If waste material (greater than 1 percent of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.1.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

> NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

> NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Section 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Section 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Section 7.1.1.9)}}{\text{Total weight of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Section 7.1.1.9 is equal to or greater than 0.5 percent, then proceed either to Section 7.1.3 to determine whether the solid material requires particle size reduction or to Section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Section 7.1.1.9 is less than 0.5 percent, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed and to Section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 ± 20 degrees C until two successive weighing yield the same value within ± 1 percent. Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Wt. of dry waste + filter) - tared wt. of filter}}{\text{Initial wt. of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5 percent, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed, and to Section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5 percent, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 7.1.3) and determine the appropriate extraction fluid (Section 7.1.4). If only the volatile TCLP is to be performed, see the note in Section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm2 , or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions musts be taken (see Section 7.3.6).

> NOTE: Surface area criteria are meant for filamentous (e.~., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5 percent and if the sample will be extracted for nonvolatile constituents (Section 7.2), determine the appropriate fluid (Section 5.7) for the nonvolatiles extraction as follows:

> NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1 (Section 5.7.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to Section 7.3.

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is less than 5.0, use extraction fluid #1. Proceed to Section 7.2.

7.1.4.3 If the pH from Section 7.1.4.2 is greater than 5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50 degrees C, and hold at 50 degrees C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is less than 5.0, use extraction fluid #1. If the pH is greater than 5.0, use extraction fluid #2. Proceed to Section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation (Sections 7.1.1 - 7.1.4) was determined to be 100 percent solid at Section 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Section 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Section 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Section 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Section 7.2.10 of the nonvolatile TCLP extraction.

Procedure When Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration e.g., is 100 percent solid, see Section 7.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to Section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains less than 0.5 percent dry solids (Section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing greater than 0.5 percent dry solids (Sections 7.1.1 or 7.1.2), use the percent solids information obtained in Section

7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Section 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 degrees C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample

NOTE: If waste material (greater than 1 percent of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.2.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (Le., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See Section 7.2.12) or stored at 4 degrees C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the waste contains less than 0.5 percent dry solids (see Section 7.1.2), proceed to Section 7.2.13. If the waste contains greater than 0.5 percent dry solids (see Section 7.1.1 or 7.1.2), and if particle size reduction of the solid was needed in Section 7.1.3, proceed to Section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 7.2.11.

7.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

> NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Section 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2 degrees C during the extraction period.

> NOTE; As agitation continues; pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filters) shall be acid-washed (see Section 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the TCLP extract as follows:

7.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.2.12 is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.2 If compatible e. ., multiple phases will not result on combination), combine the filtered liquid resulting from Section 7.2.12 with the initial liquid phase of the waste obtained in Section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Section 7.2.7, is not or may not be compatible with the filtered liquid resulting from Section 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCCLP extract, and combine the results mathematically, as described in Section 7.2.14.

7.2.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots musts be acidified with nitric acid to pH less than 2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots musts be stored under refrigeration (4 degrees C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ± 0.5 percent), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).

C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second place (mg/L).

7.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles are Involved

Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes ~., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.'

Do not allow the waste, the initial phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4 degrees C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (See Section 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis.. The containers listed in Section 4.6 are recommended for use under the conditions stated in Sections 4.6.1 - 4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 7.3, Section 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the waste is 100 percent solid (see Section 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Section 7.3.5.

7.3.4 If the waste contains less than 0.5 percent dry solids (Section 7.1.2), the liquid portion of waste, after filtration, is defined as the TCLCP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing greater than or equal to 0.5 percent dry solids (Sections 7.1.1 and/or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For wastes containing less than 5 percent solids (see Section 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing greater than or equal to 5 percent solids (see Section 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Section 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle size reduction of the solid portion of the waste was required in Section 7.1.3, proceed to Section 7.3.6. If particle size reduction was not required in Section 7.1.3, proceed to Section 7.3.7.

7.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid' portion of the waste to a surface area or particle size as described in Section 7.1.3. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4 degrees C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to Section 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

> NOTE: If waste material (greater than 1 percent of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Section 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 degrees C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100 percent solid (see Section 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Section 7.3.12.

7.3.9 Attach the evacuated pre-weighted filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 5O psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

> NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

> NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained less than 0.5 percent dry solids (see Section 7.1.2), this filtrate is defined as the TCCLP extract and is analyzed directly. Proceed to Section 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (See Sections 7.3.13 through 7.3.15) or stored at 4 degrees C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \text{ x percent solids}_{(\text{Section 7.1.1})} \text{ x weight of waste filtered}_{(\text{Section 7.3.4 or 73.8})}}{100}$$

7.3.12 The following Sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Section 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the, extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary agitation apparatus (if it is not already there) and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 ± 2 degrees C during agitation.

7.3.13 Following the 18 ± 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i-e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Section 4.2.1, and perform II, the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container i.e., TEDLAR® I bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Section 7.3.9. All extract shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Sections 4.6 and 7.3.1).

> NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.3.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.3.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Section 7.3.13 and the initial liquid phase (Section 7.3.9) are collectively defined as the TCLP extract.

7.3.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4 degrees C until analyzed. Analyze the III TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5 percent), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

8.0 QUALITY ASSURANCE

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel.

8.2 A matrix spike shall be performed for each waste type (e~., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to demonstrate teat the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

8.2.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

percentR (percentRecovery) -100 $(X_S - X_u)/K$

where:
X_S = measured value for the spiked sample,
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50 percent and the concentration does not exceed the regulatory level, and (2) the concentration of the contaminant measured in the extract is within 20 percent of the appropriate regulatory level.

8.4.1 The method of standard additions shall be employed as the internal' calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The fourth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50 percent of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100 percent and 150 percent of the expected concentration of the sample. All four aliquots are maintained at the same final volume by ' adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependent variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentrations as the dependent variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo TCLP extraction within the following time periods:'

SAMPLE MAXIMUM HOLDING TIMES [Days] _				
	From: Field Collection To: TCLP extraction	From: TCLP Extraction To: Preparative extraction	From: Preparative Extraction To: Determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not-:applicable

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.0 METHOD PERFORMANCE

9.1 Ruggedness. Two ruggedness studies have been performed to determine the effect of various perturbations on specific elements of the TCLP protocol. Ruggedness testing determines the sensitivity of small procedural variations which might be expected to occur during routine laboratory application.

9.1.1 Metals - The following conditions were used when leaching a waste for metals analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Extraction time	16 hours vs. 18 hours
Headspace	20 percent vs. 60 percent
Buffer #2 acidity	190 meq vs. 210 meq
Acid-washed filters	yes vs. no
Filter type	0.7 µm glass fiber vs. 0.45 µm vs. polycarbonate
Bottle type	borosilicate vs. flint glass

Of the seven method variations examined, acidity of the extraction fluid had the greatest impact on the results. Four of 13 metals from an API separator sludge/electroplating waste (API/EW) mixture and two of three metals from an ammonia lime still bottom waste were extracted at higher levels by the more acidic buffer. Because of the sensitivity to pH changes, the method requires that the extraction fluids be prepared so that the final pH is within ± 0.5 units as specified.

9.1.2 Volatile Organic Compounds - The following conditions were used when leaching a waste for VOC analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Headspace	0 percent vs. 5 percent
Buffer #1 acidity	60 meq vs. 80 meq
Method of storing extract	Syringe vs. Tedlar® bag
Aliquotting	yes vs. no
Pressure behind piston	0 psi vs. 20 psi

None of the parameters had a significant effect on the results of the ruggedness test.

9.2 Precision. Many TCLP precision (reproducibility) studies have been performed, and have shown that, in general, the precision of the TCLP is comparable to or exceeds that of the EP toxicity test and that method precision is adequate. One of the more significant contributions to poor precision appears to be related to sample homogeneity and inter--°laboratory variation (due to the nature of waste materials).

9.2.1 Metals - The results of a multi-laboratory study are shown in Table 6, and indicate that a single analysis of a waste may not be adequate for waste characterization and identification requirements.

9.2.2 Semi-Volatile Organic Compounds - The results of two studies are shown in Tables 7 and 8. Single laboratory precision was excellent with greater than 90 percent of the results exhibiting an RSD less than 25 percent. Over 85 percent of all individual compounds in the multi-laboratory study ell in the RSD range of 20 - 120 percent. Both studies concluded that the TCLP provides adequate precision. It was also determined that the high acetate content of the extraction fluid did not present problems <u>(i.e.,</u> column degradation of the gas chromatography for the analytical conditions used.

9.2.3 Volatile Organic Compounds - Eleven laboratories participated in a collaborative study of the use of the ZHE with two waste types which were fortified with a mixture of VOCs. The results of the collaborative study are shown in Table 9. Precision results for VOCs tend to occur over a considerable range. However, the range and mean RSD compared very closely to the same collaborative study metals results in Table 6. Blackburn and Show concluded that at the 95 percent level of significance: 1) recoveries among laboratories were statistically similar, 2) recoveries did not vary significantly between the two sample types, and 3) each laboratory showed the same pattern of recovery for each of the two samples.

10.0 REFERENCES

1. Blackburn, W.B. and Show, I. "Collaborative Study of the Toxicity Characteristics Leaching Procedure (TCLP)." Draft Final Report, Contract No. 68-03-1958, S-Cuted, November 1986.

2. Newcomer, L.R., Blackburn, W.B., Kimmell, T.A. "Performance of the Toxicity Characteristic Leaching Procedure." Wilson Laboratories, S-Cubed, U.S. EPA, December 1986.

3. Williams, L.R., Francis, C.W.; Maskarinec, M.P., Taylor D.R., and Rothman, N. "Single-Laboratory Evaluation of Mobility Procedure for Solid Waste." EMSL, ORNL, S Cubed, ENSECO.

Table 1
Volatile Analytes[1,2]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2,-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	133-20-7

[1]When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

[2] Benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene, and vinyl chloride are toxicity characteristic constituents.

Table 2.
Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S) 8-vessel extractor (DC20) 12-vessel extractor (DC20B) 24-vessel extractor (DC240C)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2-BRE) 4-vessel (3740-4-BRE) 6-vessel (3740-6-BRE) 8-vessel (3740-8-BRE) 12-vessel (3740-12-BRE) 24-vessel (3740-24-BRE)
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitemore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (SVRE) 6-vessel (6VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 2-liter bottle extractor (YT31 ORAHW)

[1]Any device that rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

Table 3.

Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C 102, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing2	Whitemore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30090HW, Gas Pressure Device
Environmental Machine and Design; Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOXI, Gas Pressure Device
Gelman Science	Ann Arbor, MI (800) 521-1520	15400 Gas Pressure Device

[1]Any device that meets the specifications listed in Section 4.2.1 of the method is suitable.

[2]This device uses a 110 mm filter.

Table 4.
Suitable Filter Holders[1]

Company	Model/ Location	Catalogue No.	Size
Nucleopore Corporation	Pleasanton, CA	425910	124 mm
	(800) 882-7711	410400	47 mm
Micro Filtration Systems	Dublin, CA	302400	142 mm
	(800) 334-7132	311400	-47 mm
	(41 S) 828-6010		
Millipore Corporation	Bedford, MA	XT30142HW	124 mm
	(800) 225-3384	XX1004700	47 mm

[1]Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5.
Suitable Filter Media[1]

Company	Location	Model	Pore Size (µm)
Millipore Corporation (800) 225-3384	Bedford, MA	AP40	0.7
Nucleopore Corporation (415) 463-2530	Pleasanton, CA	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7
Gelman Science	Ann Arbor, MI (800) 521-1520	66256 (90mm) 66257 (142mm)	0.7

[1]Any filter that meets the specifications in Section 4.4 of the Method is suitable.

Table 6. Mufti-Laboratory TCLP Metals, Precision

Waste	Extraction Fluid	Metal	X	S	percentRSD
Ammonia	#1	Cadmium	0.053	0.031	60
Lime Still	#2		0.023	0.017	76
Bottoms	#1	Chromium	0.015	0.0014	93
	#2		0.0032	0.0037	118
	#1	Lead	0.0030	0.0027	90
	#2		0.0032	0.0028	87
API/EW-	#1	Cadmium	0.0046	0.0028	61
Mixture	#2		0.0005	0.0004	77
	#1	Chromium	0.0561	0.0227	40
	#2		0.105	0.018	17
	#1	Lead	0.0031	0.0031	100
	#2		0.0124	0.0136	110
Fossil	#1	Cadmium	0.080	0.069	86
Fuel Fly	#2		0.093	0.067	72
Ash	#1	Chromium	0.017	0.014	85
	#2		0.070	0.040	57
	#1	Lead	0.0087	0.0074	85
	#2		0.0457	0.0083	18
percentRSD Range =17 - 118 Mean percentRSD = 74					

NOTE: X = Mean results from 6 - 12 different laboratories
Units = mg/L
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 7. Single-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	X	S	Percent RSD
Ammonia	Phenol	#1	19000	2230	11.6
Lime Still		#2	19400	929	4.8
Bottoms	2-Methylphenol	#1	2000	297	14.9
		#2	1860	52.9	2.8
	4-Methylphenol	#1	7940	1380	17.4
		#2	7490	200	2.7
	2,4-Dimethylphenol	# 1	321	46.8	14.6
		#2	307	45.8	14.9
	Naphthalene	#1	3920	413	10.5
		#2	3827	176	4.6
	2-Methylnaphthalene	#1	290	44.8	15.5
		#2	273	19.3	7.1
	Dibenzofuran	#1	187	22.7	12.1
		#2	187	7.2	3.9
	Acenaphthylene	#1	703	89.2	12.7
		#2	663	20.1	3.0
	Fluorene	#1	151	17.6	11.7
		#2	156	2.1	1.3
	Phenanthrene	#1	241	22.7	9.4
		#2	243	7.9	3.3
	Anthracene	#1	33.2	6.19	18.6
		#2	34.6	1.55	4.5
	Fluoranthrene	#1	25.3	1.8	7.1
		#2	26.0	1.8	7.1
API/EW	Phenol	#1	40.7	13.5	33.0
Mixture		#2	19.0	1.76	9.3
	2,4-Dimethylphenol	#1	33.0	9.35	28.3
		#2	43.3	8.61	19.9
	Naphthalene	#1	185	29.4	15.8
		#2	165	24.8	15.0
	2-Methylnaphthalene	#1	265	61.2	23.1
		#2	200	18.9	9.5
					percentRSDRange = 1 - 33 Mean percentRSD - 12

NOTE: Units = µg/L

Extractions were performed in triplicate

All results were at least 2x the detection limit

Extraction Fluid # 1 = pH 4.9

#2 = pH 2.9

Table 8. Mufti-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	X	S	Percent RSD
Ammonia Lime	BNAs	#1	10043	7680	76.5
Still Bottoms (A)		#2	10376	6552	63.1
API/EW	BNAs	#1	1624	675	41.6
Mixture (B)		#2	2074	1463	70.5
Fossil Fuel	BNAs	#1	750	175	23.4
Fly Ash (C)		#2	739	342	46.3
					Mean percentRSD = 54

NOTE: Units = µg/L
X = Mean results from 3 - 10 labs
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

percentRSD Range for Individual Compounds

A, #1	0 - 113
A, #2	28 - 108
B, #1	20 - 156
B, #2	49 - 128
C, #1	36 - 143
C, #2	61 - 164

Table 9. Mufti-Laboratory (11 Labs) VOCs, Precision

Waste	Compound	X	S	percentRSD
Mine Tailings	Vinyl chloride	6.36	6.36	100
	Methylene chloride	12.1	11.8	98
	Carbon disulfide	5.57	2.83	51
	l,l-Dichloroethene	21.9	27.7	127
	1,1-Dichloroethane	31.4	25.4	81
	Chloroform	46.6	29.2	63
	1,2,-Dichloroethane	47.8	33.6	70
	2-Butanone	43.5	36.9	85
	1,1,1-Trichloroethane	20.9	20.9	100
	Carbon tetrachloride	12.0	8.2	68
	Trichloroethene	24.7	21.2	86
	1,1,2-Trichloroethene	19.6	10.9	56
	Benzene	37.9	28.7	76
	1,1,2,2-Tetrachloroethane	34.9	25.6	73
	Toluene	29.3	11.2	38
	Chlorobenzene	35.6	19.3	54
	Ethylbenzene	4.27	2.80	66
	Trichlorofluoromethane	3.82	4 40	115
	Acrylonitrile	76.7	110.8	144
Ammonia Lime Still Bottoms	Vinyl chloride	5.00	4.71	94
	Methylene chloride	14.3	13.1	92
	Carbon disulfide	3.37	2.07	61
	1,1,-Dichoroethene	52.1	38.8	75
	l,l-Dichloroethane	52.8	25.6	49
	Chloroform	64.7	28.4	44
	1,2-Dichloroetehane	43.1	31.5	73
	2-Butanone	59.0	39.6	67
	1,1,1-Trichloroethane	53.6	40.9	76
	Carbonn tetrachlordie	7.10	6.1	86
	Trichloroethene	57.3	34.2	60
	1,1,2-Trichloroethene	6.7	4.7	70
	Benzene	61.3	26.8	44
	1;1,2,2-Tetrachloroethane	3.16	2.1	66
	Toluene	69.0	18.5	27
	Chlorobenzene	71.8	12.0	17
	Ethylbenzene	3.70	2.2	58
	Trichlorofluoromethane	4.05	4.8	119
	Acrylonitrile	29.4	34.8	118
				percentRSD Range = 17 - 144
				Mean percentRSD = 75

NOTE: Units= µg/L

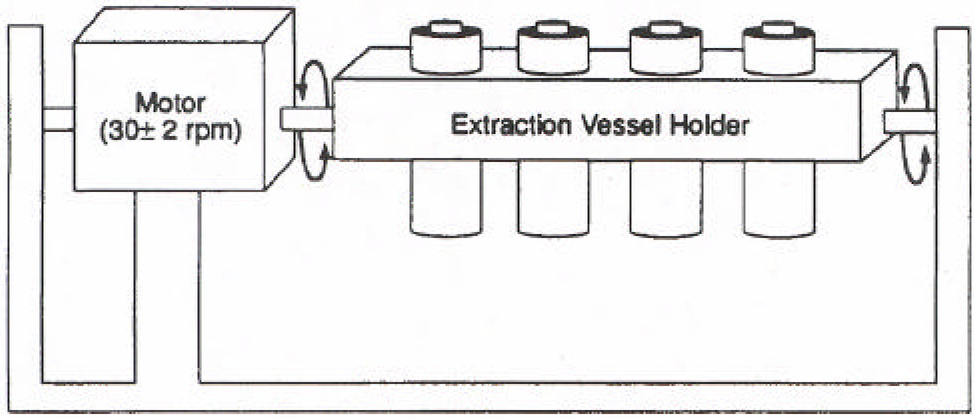


Figure 1. Rotary Agitation Apparatus

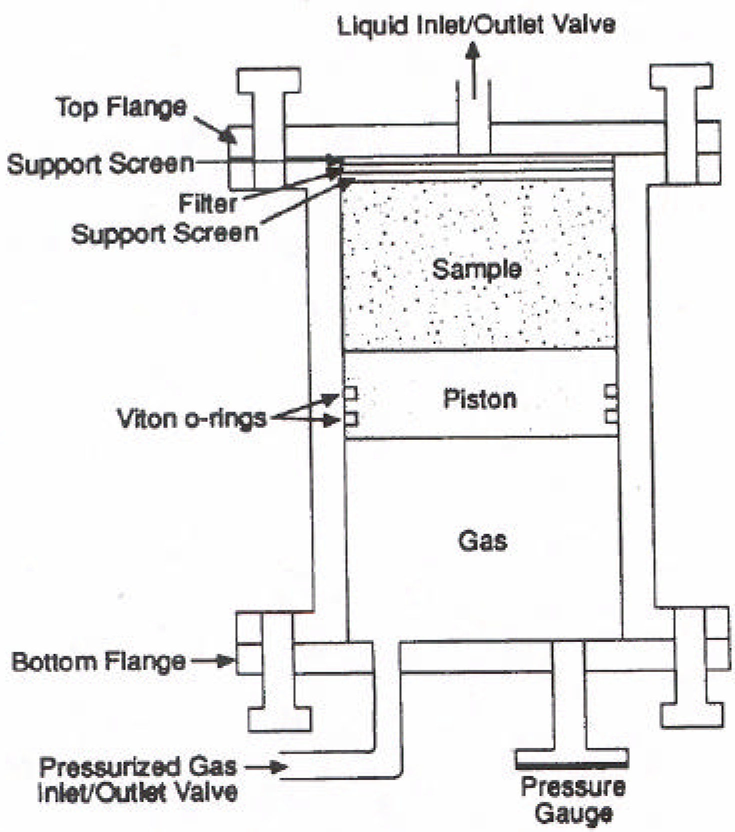
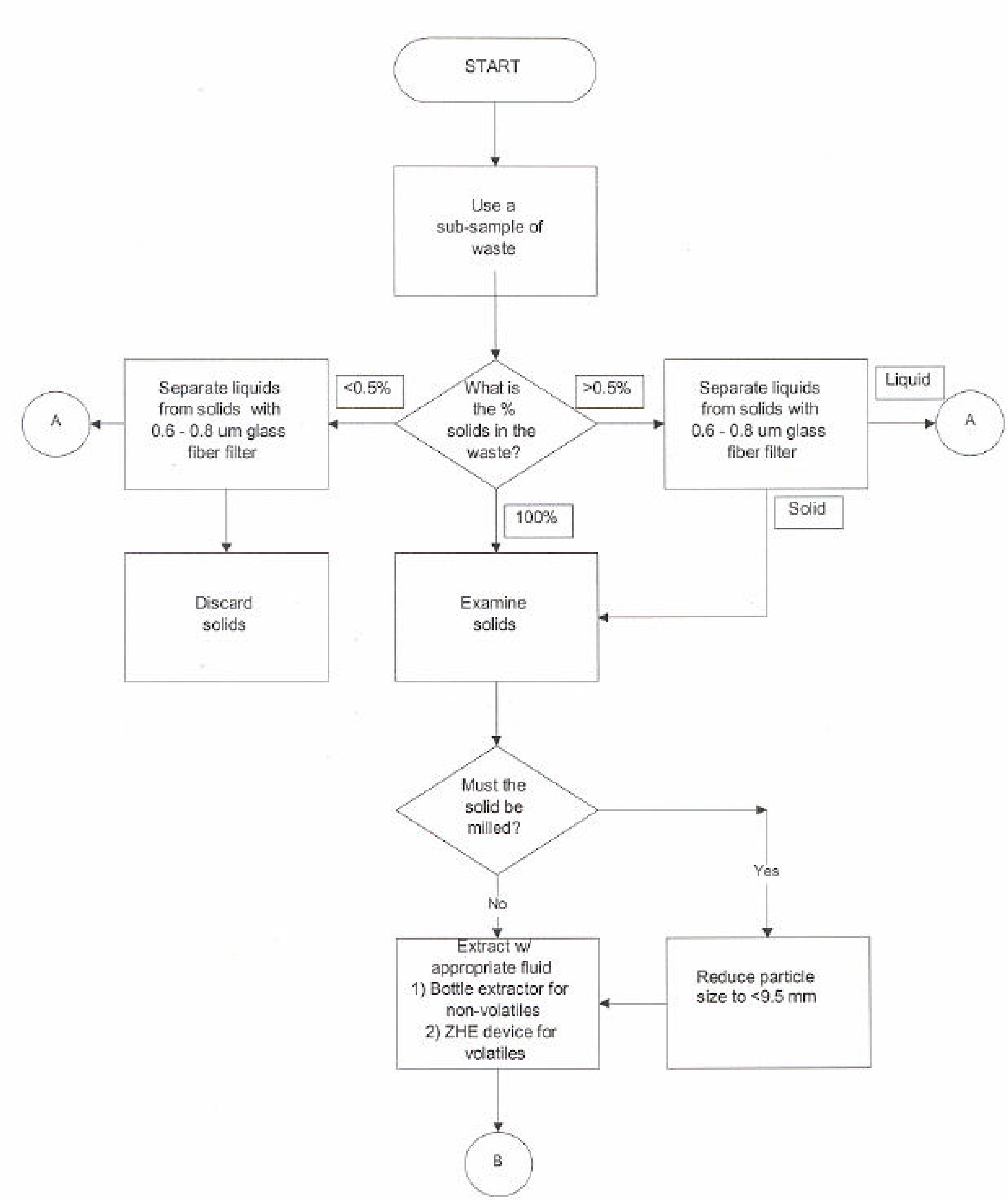
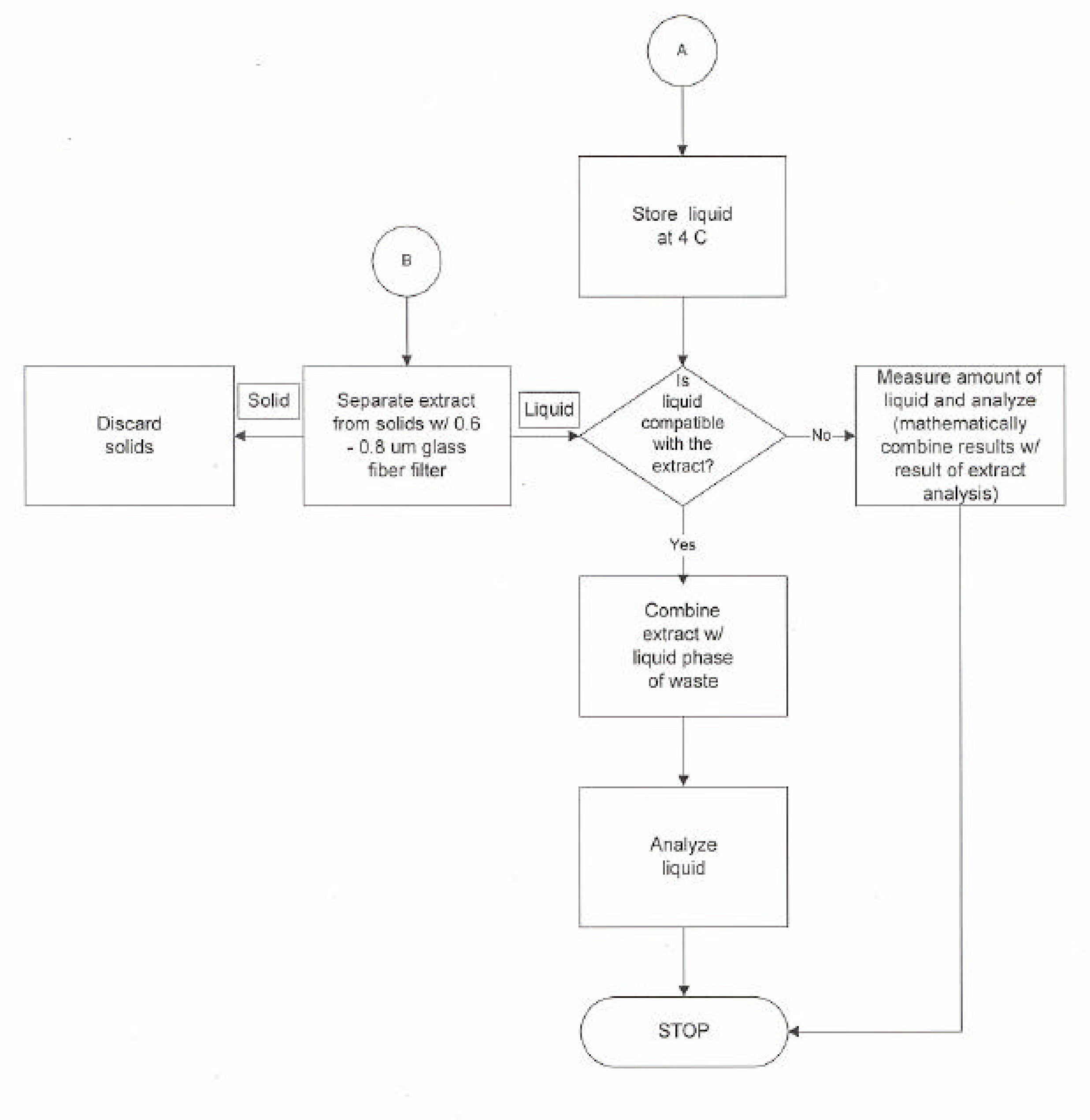


Figure 2. Zero-Headspace Extractor (ZHE)

Method 1311
Toxicity Characteristic Leachate Procedure



Method 1311
Toxicity Characteristic Leachate Procedure continued



3.F.1 METHOD 9076

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY PRODUCTS BY OXIDATIVE COMBUSTION AND MICROCOULOMETRY

1.0 SCOPE AND APPLICATION

1.1 This test method covers the determination of total chlorine in new and used oils, fuels and related materials, including crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by oxidative combustion and microcoulometry. The chlorine content of petroleum products is often required prior to their use as a fuel.

1.2 The applicable range of this method is from 10 to 10,000 µg/g chlorine.

2.0 SUMMARY OF METHOD

2.1 The sample is placed in a quartz boat at the inlet of a high-temperature quartz combustion tube.-An inert carrier gas such as argon, carbon dioxide, or nitrogen sweeps across the inlet while oxygen flows into the center of the combustion tube. The boat and sample are advanced into a vaporization zone of approximately 300 degrees C to volatilize the light ends. Then the boat is advanced to the center of the combustion tube, which is at 1,000 degrees C. The oxygen is diverted to pass directly over the sample to oxidize any remaining refractory material. All during this complete combustion cycle, the chlorine is converted to chloride and oxychlorides, which then flow into an attached titration cell where they quantitatively react with silver ions. The silver ions thus consumed are coulometrically replaced. The total current required to replace the silver ions is a measure of the chlorine present in the injected samples.

2.2 The reaction occurring in the titration cell as chloride enters is:

$$CI^- + Ag^+ \dashrightarrow AgCI \qquad (1)$$

The silver ion consumed in the above reaction is generated coulometrically thus:

$$Ag^0 \dashrightarrow Ag^+ + e- \qquad (2)$$

2.3 These microequivalents of silver are equal to the number of micro-equivalents of titratable sample ion entering the titration cell.

3.0 INTERFERENCES

3.1 Other titratable halides will also give a positive response. These titratable halides include **HBr and HI (HOBr + HOI** do not precipitate silver). Because these oxyhalides do not react in the titration cell, approximately 50% microequivalent response is detected from bromine and iodine.

3.2 Fluorine as fluoride does not precipitate silver, so it is not an interferant nor is it detected.

3.3 This test method is applicable in the presence of total sulfur concentrations of up to 10,000 times the chlorine level.

4.0 APPARATUS AND MATERIALS[6]

4.1 Combustion furnace. The sample should be oxidized in an electric furnace capable of maintaining a temperature of 1,000 degrees C to oxidize the organic matrix.

4.2 Combustion tube, fabricated from quartz and constructed so that a sample, which is vaporized completely in the inlet section, is swept into the oxidation zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube connects to a boat insertion device where the sample can be placed on a quartz boat by syringe, micropipet, or by being weighed externally. Two gas ports are provided, one for an inert gas to flow across the boat and one for oxygen to enter the combustion tube.

4.3 Microcoulometer, Stroehlein Coulomat 702 CL or equivalent, having variable gain and bias control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. The microcoulometer output signal shall be proportional to the generating current. The microcoulometer may have a digital meter and circuitry to convert this output signal directly to a mass of chlorine (e.g., nanograms) or to a concentration of chlorine (e.g., micrograms of chlorine or micrograms per gram).

4.4 Titration cell. Two different configurations have been applied to coulometrically titrate chlorine for this method. III

4.4.1 Type I uses a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain constant silver ion concentration and an inlet for a gaseous sample from the pyrolysis tube. The sensor, reference, and anode electrodes are silver electrodes. The cathode electrode is a platinum wire. The reference electrode resides in a saturated silver acetate half-cell. The electrolyte contains 70 percent acetic acid in water.

4.4.2 Type II uses a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain

6 Any apparatus that meets the performance criteria of this section may be used to conduct analyses by this methodology. Three commercial analyzers that fulfill the requirements for apparatus Steps 4.1 through 4.4 are: Dohrmann Models DX-20B and MCTS-20 and Mitsubishi Model TSX-10 available from Cosa Instrument.

constant silver ion concentration, an inlet for a gaseous sample that passes through a 95 percent sulfuric acid dehydrating tube from the pyrolysis tube, and a sealed two-piece titration cell with an exhaust tube to vent fumes to an external exhaust. All electrodes can be removed and replaced independently without reconstructing the cell assembly. The anode electrode is constructed of silver. The cathode electrode is constructed of platinum. The anode is separated from the cathode by a 10 percent KN03 agar bridge, and continuity is maintained through an aqueous 10 percent KN03 salt bridge. The sensor electrode is constructed of silver. The reference electrode is a silver/silver chloride ground glass sleeve, double junction electrode with aqueous 1M KN03 in. the outer chamber and aqueous 1M KCl in the inner chamber.

4.5 Sampling syringe, a microliter syringe of 10 AL capacity capable of accurately delivering 2 to 5 /µL of a viscous sample into the sample boat.

4.6 Micropipet, a positive displacement micropipet capable of accurately delivering 2 to 5 µL of a viscous sample into the sample boat.

4.7 Analytical balance. When used to weigh a sample of 2 to 5 mg onto the boat, the balance shall be accurate to + 0.01 mg. When used to determine the density of the sample, typically 8 g per 10 mL, the balance shall be accurate to + 0.1 g.

4.8 Class A volumetric flasks: 100 mL.

5.0 REAGENTS

5.1 Purity of Reagents. Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Acetic acid, $CH_3\ CO_2H$. Glacial.

5.4 Isooctane, $(CH_3)_2\ CHCH_2\ C(CH_3)_3$ (2,2,4-Trimethylpentane).

5.5 Chlorobenzene, C_6H_5 C1.

5.6 Chlorine, standard stock solution - 10,000 ng Cl/µL, weigh accurately 3.174 g of chlorobenzene into 100-mL Class A volumetric flask. Dilute to the mark with isooctane.

5.7 Chlorine, standard solution. 1,000 ng Cl/µL, pipet 10.0 mL of chlorine stock solution (Sec. 5.6) into a 100-mL volumetric flask and dilute to volume with isooctane.

5.8 Argon, helium, nitrogen, or carbon dioxide, high-purity grade (HP) used as the carrier gas. High-purity grade gas has a minimum purity of 99.995 percent.

5.9 Oxygen, high-purity grade (HP), used as the reactant gas.

5.10 Gas regulators. Two-stage regulator must be used on the reactant and carrier gas.

5.11 Cell Type 1.

5.11.1 Cell electrolyte solution. 70 percent acetic acid: combine 300 mL reagent water with 700 mL acetic acid (Sec. 5.3) and mix well.

5.11.2 Silver acetate, CH3 COZ Ag. Powder purified for saturated reference electrode.

5.12 Cell Type 2.

5.12.1 Sodium acetate, $CH_3 C0_2$ Na.

5.12.2 Potassium nitrate, $KN0_3$.

5.12.3 Potassium chloride, KCI.

5.12.4 Sulfuric acid (concentrated), $H_2 S0_4$.

5.12.5 Agar, (jelly strength 450 to 600 g/cm^2).

5.12.6 Cell electrolyte solution - 85 percent acetic acid: combine 150 mL reagent water with 1.35 g sodium acetate (Sec. 5.12.1) and mix well; add 850 mL acetic acid (Sec. 5.3) and mix well.

5.12.7 Dehydrating solution - Combine 95 mL sulfuric acid (Sec. 5.12.4) with 5 mL reagent water and mix well.

CAUTION: This is an exothermic reaction and may proceed with bumping unless controlled by the addition of sulfuric acid. Slowly add sulfuric acid to reagent water. Do not add water to sulfuric acid.

5.12.8 Potassium nitrate (10 percent), KN03 . Add 10 g potassium nitrate (Sec. 5.12.2) to 100 mL reagent water and mix well.

5.12.9 Potassium nitrate (1M), KN03 . Add 10.11 g potassium nitrate (Sec. 5.12.2) to 100 mL reagent water and mix well.

5.12.10 Potassium chloride (1M), KCI. Add 7.46 g potassium chloride (Sec.

5.12.3) to 100 ml, reagent water and mix well.

5.12.11 Agar bridge solution - Mix 0.7 g agar (Sec. 5.12.5), 2.5g potassium nitrate (Sec. 5.12.2), and 25 mL reagent water and heat to boiling.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Because the collected sample will be analyzed for total halogens, it should be kept headspace free and refrigerated prior to preparation and to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

6.3 Laboratory subsampling of the sample should be performed on a well-mixed sample of oil.

7.0 PROCEDURES

7.1 Preparation of apparatus.

7.1.1 Setup the analyzer as per the equipment manufacturer's instructions.

7.1.2 Typical operating conditions: Type 1.

Furnace temperature ....1,000 degrees C
Carrier gas flow ....43 cm^3/min
Oxygen gas flow ....160 cm^3/min
Coulometer Bias ....250 mV
Gain...25 percent

7.1.3 Typical operating conditions: Type 2.

Furnace temperature	H-1 850 degrees C
Furnace temperature	H-2 1,000 degrees C
Carrier gas flow	250 cm^3/min
Oxygen gas flow	250 cm^3/min
Coulometer End point potential (bias)	300 mV
Gain G-1	1.5 coulombs/ change in mV
Gain G-2	3.0 coulombs/ change in mV
Gain G-3	3.0 coulombs/ change in mV
ES-1 (range 1)	25 mV
ES-2 (range 2)	30 mV

NOTE: Other conditions may be appropriate. Refer to the instrumentation manual.

7.2 Sample introduction.

7.2.1 Carefully fill a 10-µL syringe with 2 to 5 µL of sample depending on the expected concentration of total chlorine. Inject the sample through the septum onto the cool boat, being certain to touch the boat with the needle tip to displace the last droplet.

7.2.2 For viscous samples that cannot be drawn into the syringe barrel, a positive displacement micropipet may be used. Here, the 2-5 µL of sample is placed on the boat from the micropipet through the opened hatch port. The same technique as with the syringe is used to displace the last droplet into the boat. A tuft of quartz wool in the boat can aid in completely transferring the sample from the micropipet into the boat.

NOTE: Dilution of samples to reduce viscosity is not recommended due to uncertainty about the solubility of the sample and its chlorinated constituents. If a positive displacement micropipet is not available, dilution may be attempted to enable injection of viscous samples.

7.2.3 Alternatively, the sample boat may be removed from the instrument and tared on an analytical balance. A sample of 2-5 mg is accurately weighed directly into the boat and the boat and sample returned to the inlet of the instrument.

2-5 µL = 2-5 mg

NOTE: Sample dilution may be required to ensure that the titration system is not overloaded with chlorine. This will be somewhat system dependent and should be determined before analysis is attempted. For example, the MCTS-20 can titrate up to 10,000 ng chlorine in a single injection or weighed sample, while the DX-20B has an upper limit of 50,000 ng chlorine. For 2 to 5 µL sample sizes, these correspond to nominal concentrations in the sample of 800 to 2,000 µg/g and 4,000 to 10,000 µg/g, respectively. If the system is overloaded, especially with inorganic chloride, residual chloride may persist in the system and affect results of subsequent samples. In general, the analyst should ensure that the baseline returns to normal before running the next sample. To speed baseline recovery, the electrolyte can be drained from the cell and replaced with fresh electrolyte.

NOTE: To determine total chlorine, do not extract the sample either with reagent water II or with an organic solvent such as toluene or isooctane. This may lower the inorganic chlorine content as well as result in losses of volatile solvents.

7.2.4 Follow the manufacturer's recommended procedure for moving the sample and boat into the. combustion tube.

7.3 Calibration and standardization.

7.3.1 System recovery - The fraction of chlorine in a standard that is titrated should be verified every 4 hours by analyzing the standard solution (Sec. 5.7). System recovery is typically 85 percent or better. The pyrolysis tube should be replaced whenever system recovery drops below 75 percent.

NOTE: The 1,000 µg/g system recovery sample is suitable for all systems except the MCTS-20 for which a 100 µg/g sample should be used.

7.3.2 Repeat the measurement of this standard at least three times.

7.3.3 System blank - The blank should be checked daily with isooctane. It is typically less than 1 µg/g chlorine. The system blank should be subtracted from both samples and standards.

7.4 Calculations.

7.4.1 For systems that read directly in mass units of chloride, the following equations apply:

$$\text{Chlorine, µg/g (wt/wt)} = \frac{\text{Display}_s}{(V_s)(D_s)(RF)} - B \qquad (3)$$

or

$$\text{Chlorine, pg/g (wt/wt)} = \left| \frac{\text{Displays}}{(M)} - B \right| \qquad (4)$$

where:

Display = Integrated value in nanograms (when the integrated values are displayed in micrograms, they must be multiplied by 10^3)

Display_B = blank measurement

Display_s = sample measurement

V = Volume of sample injected in microliters

V_B = blank volume

V_S = sample volume

D = Density of sample, grams per cubic centimeters

D_B = blank density

D_S = sample density

RIF = Recovery factor = ratio of chlorine = determined in standard minus the system blank, divided by known standard content $= \dfrac{\text{Found - Blank}}{\text{Known}}$

B = System blank, µg/g chlorine $= \dfrac{\text{Display}_B}{(V_B)\,(D_B)}$

M = Mass of sample, mg

7.4.2 Other systems internally compensate for recovery factor, volume, density, or mass and blank, and thus read out directly in parts per million chlorine units. Refer to instrumentation manual.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Each sample should be analyzed twice. If the results do not agree to within 10 percent, expressed as the relative percent difference of the results, repeat the analysis.

8.3 Analyze matrix spike and matrix spike duplicates - spike samples with a chlorinated organic at a level of total chlorine commensurate with the levels being determined. The spike recovery should be reported and should be between 80 and 120 percent of the expected value. Any sample suspected of containing greater than 25 percent water should also be spiked with organic chlorine.

9.0 METHOD PERFORMANCE

9.1 These data are based on 66 data points obtained by 10 laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. One laboratory and four additional data points were determined to be outliers and are not included in these results.

9.2 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method the following values only in 1 case in 20 (see Table 1):

Repeatability = 0.137 x*

*where x is the average of two results in µg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

Reproducibility = 0.455 x*

*where x is the average value of two results in µg/g.

9.3 Bias. The bias of this test method varies with concentration, as shown in Table 2:

Bias = Amount found - Amount expected

10.0 REFERENCE

1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels." Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA80. July 1988.

2. Rohrobough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

3. Standard Instrumentation, 3322 Pennsylvania Avenue, Charleston, WV 25302.

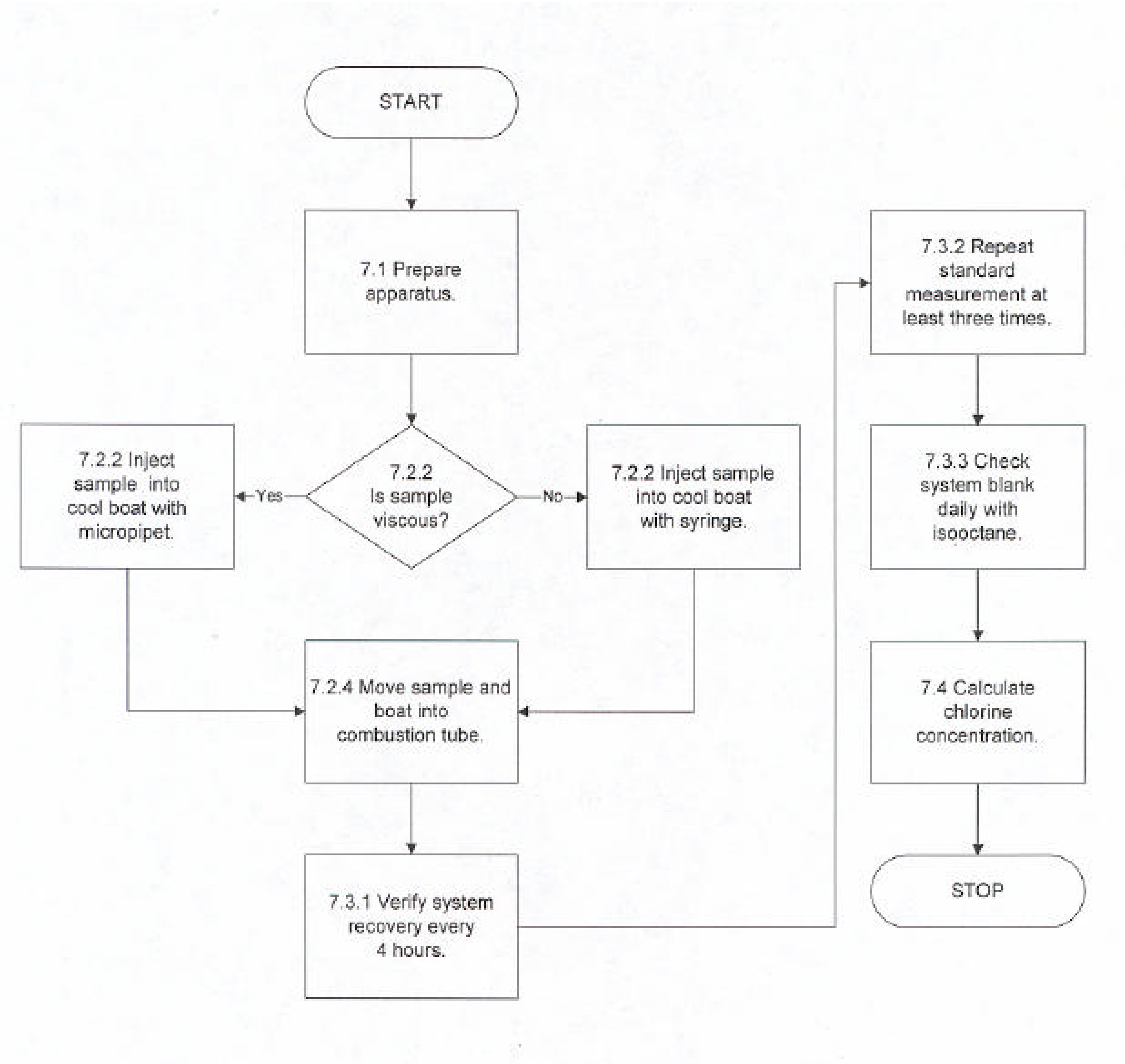
TABLE 1.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY MICROCOULOMETRIC TITRATION

Average value µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	69	228
1,000	137	455
1, 500	206	683
2,000	274	910
2,500	343	1,138
32000	411	1,365

TABLE 2.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY MICROCOULOMETRIC TITRATION

Amount expected, µg/g	Amount found µg/g	Bias, µg/g	Percent bias
320	312	-8	-3
480	443	-37	-8
920	841	-79	-9
1,498	1,483	-15	-1
1,527	1,446	-81	-5
3,029	3,016	-13	.0
3,045	2,916	-129	-4

METHOD 9076 TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS BY OXIDATIVE COMBUSTION AND MICROCOULOMETRY



APPENDIX 3

Analytical Methods for Designating Dangerous Waste

A. Sample Containers and Sample Preservation for Appendix 3 Analytical Methods
B. Analyses for the Ignitability Characteristic

1. SW-846 Method 1010

2. SW-846 Method 1020A

C. Analyses for the Corrosivity Characteristic

1. SW-846 Method 9040B
2. SW-846 Method 9045C
3. SW-846 Method 1110

D. Analyses for the Reactivity Characteristic

1. SW-846 Method 7.3.3.2
2. SW-846 Method 7.3.4.2
3. SW-846 Method 9014
4. SW-846 Method 9034

E. Analysis for the Toxicity Characteristic

1. SW-846 Method 1311

F. Analysis for the Criteria of Persistence: Halogenated Organic Carbon Screen

1. SW-846 Method 9076

3.A Sample Containers and Sample Preservation

For the analysis in Appendix 3, the following chart contains information pertaining to sample containers and sample preservation:

Analysis		Matrix	Container	Preservative
SW-846	**Other methods**			
Method 1010: Flash Point (Pensky - Martens)	ASTM Standard D-93-79 or D-93-80	Solids greater than 20 glass jar percent by weight	glass jar	Cool to 4 degrees Celsius
Method 1020A: Flash Point (Setaflash)	ASTM Standard D-3278-78	Solids less than 20 percent by weight	glass jar	Cool to 4 degrees Celsius
Method 9040B: pH	• Standard Methods[1] 4500H • EPA Method' 150.1	Solids less than 20 percent by weight	glass jar or polyethylene	Cool to 4 degrees Celsius
Method 9045C: pH		Solids greater than 20 percent by weight	glass jar	Cool to 4 degrees Celsius
Method 1110: Corrosivity Towards Steel	NACE3 Standard TM-01-69	Aqueous and non-aqueous liquids	glass jar	Cool to 4 degrees Celsius
Method 7.3.3.2: Reactive Cyanide		Solids	glass jar	Cool to 4 degrees Celsius
Method 7.3.3.2: Reactive Cyanide	Standard Methods[33] 4500CN-C, 4500CN-E, and 450OCN-1	Aqueous liquids	amber polyethylene	• Cool to 4 degrees Celsius • NaOH to pH greater than 12 • Ascorbic acid

[1] *Standard Methods for the Examination of Water and Wastewater,* 18th Edition.
[2] *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater,* EPA 600/4-79-020
[3] National Association of Corrosion Engineers

Analysis		Matrix	Container	Preservative
SW-846	Other methods			
Method 7.3.4.2: Reactive Sulfide		Solids	glass jar	Cool to 4 degrees Celsius
Method 7.3.4.2: Reactive Sulfide	• Standard Methods" 41 l OB • EPA Method34 150.1	Aqueous liquids	polyethylene	• Cool to 4 degrees Celsius • NaOH to pH greater than 9 • Zinc acetate
Method 1311: TCLP		Solids	glass jar	Cool to 4 degrees Celsius
Method 1311: TCLP		Aqueous and nonaqueous liquids	• 1 Liter HDPE bottle for metal analyses • 1 Liter glass jar for organic analyses	Cool to 4 degrees Celsius
Method 9076: Total Chlorine		Aqueous liquids, nonaqueous liquids, and solids	glass jar	Cool to 4 degrees Celsius
Method 8100: PAHs		Aqueous liquids, nonaqueous liquids, and solids	• 8 oz. glass jar (solids) • 1 gal. glass jar (liquids)	Cool to 4 degrees Celsius
Method 8310: PAHs		Aqueous liquids, nonaqueous liquids, and solids	• 8 oz. glass jar (solids) • 1 gal. glass jar (liquids)	Cool to 4 degrees Celsius
Method 8270C: Semivolatile organics	EPA Method 14 625	Aqueous liquids, nonaqueous liquids, and solids	• 8 oz. glass jar (solids) • 1 gal. glass jar (liquids)	Cool to 4 degrees Celsius

[33] *Standard Methods for the Examination of Water and Wastewater, 18th* Edition.
[34] *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater,* EPA 600/4-79-020

3.B.1 METHOD 1010

PENSKY-MARTINS CLOSED-CUP MPTHO IP FOR DETERMINING IGNITABILITY

1.0 SCOPE AND APPLICATION

1.1 Method 1010 uses the Pens -Mart6ns closed-cup tester to determine the flash point of liquids including those that tend to form a!, surface film under test conditions. Liquids containing non-filterable, suspended solids shall also be tested using this method.

2.0 SUMMARY OF METHOD

2.1 The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame ignites the vapor above the sample.

For further information on how to conduct a test by this method, see Reference 1 below.

3.0 METHOD PERFORMANCE

3.1 The Pensky-Martens and Set4flash Closed Testers were evaluated using five industrial waste mixtures and p-xylene. The results of this study are shown below in degrees F along with other data.

Sample	Pensky-Martens	Setaflash
12	143.7 ± 1.5	139.3 ± 2.1
22	144.7 ± 4.5	129.7 ± 0.6
32	93.7 ± 1.5	97.7 ± 1.2
42	198.0±4.0	185.3±0.6
52	119.3 ± 3.1	122.7 ± 2.5
p-xylene2	81.3 ± 1.1	79.3 ± 0.6
p-xylene3	77.7 ± O.5[a]	--
		--
Tanker oil	125, 135	
Tanker oil	180, 180	--
Tanker oil	110, 110	--
DIBK/xylene	102 ± 4[b]	107

[a]12 determinations over five-day period.
[b]75/25 v/v analyzed by four laboratories.

4.0 REFERENCES

1. D 93-80, Test Methods for Flash Point by Pensky-Martens Closed Tester, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103, 04.09, 1986.

2. Umana, M., Gutknecht, W., Salmons, C., et al., Evaluation of Ignitability Methods (Liquids), EPA/600/54-85/053, 1985.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

3.B.2 METHOD 1020

SETAFLASH **CLOSED-CUP METHOD FOR DETERMINING IGNITABILITY**

1.0 SCOPE AND APPLICATION

1.1 Method 1020 makes use of the Setaflash Closed Tester to determine the flash point of liquids that have flash points between 0 degrees and 110 degrees C (32 degrees and 230 degrees F) and viscosities lower than 150 stokes at 25 degrees C (77 degrees F).

1.2 The procedure may be used to determine whether a material will or will not flash at a specified temperature or to determine the finite temperature at which a material will flash.

1.3 Liquids that tend to form surface films under test conditions or those that contain non-filterable suspended solids shall be tested for ignitability using Method 1010 (Pensky-Martens Closed-Cup).

2.0 SUMMARY OF METHOD

2.1 By means of a syringe, 2-mL of sample is introduced through a leak-proof entry port into the tightly closed Setaflash Tester or directly into the cup which has been brought to within 3 degrees C (5 degrees F) below the expected flash point.

2.2 As a flash/no-flash test, the expected flash-point temperature may be a specification (e.g., 60 degrees C). For specification testing, the temperature of the apparatus is raised to the precise temperature of the specification flash point by slight adjustment of the temperature dial. After 1 minute, a test flame is applied inside the cup and note is taken as to whether the test sample flashes or not. If a ,repeat test is necessary, a fresh sample should be used.

2.3 For a finite flash management, the temperature is sequentially increased through the anticipated range, the test flame being applied at 5 degrees C (9 degrees F) intervals until a flash is observed. A repeat determination is then made using a fresh sample, starting the test at the temperature of the last interval before the flash point of the material and making tests at increasing 0.5 degrees C (1 degrees F) intervals.

For further information on how to conduct a test with this method, see Reference 1 below.

3.0 METHOD PERFORMANCE

See Method 1010.

4.0 REFERENCES

1. D-3278-78, Test Method for Flash Point of Liquids by Setaflash Closed Tester, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

2. Umana, M., Gutknecht, W., Salmons, C., et al., Evaluation of Ignitability Methods (Liquids), EPA/600/54-85/053, 1985.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

3. C.1 METHOD 9040B

pH ELECTROMETRIC MEASUREMENT

1.0 SCOPE AND APPLICATION

1.1 Method 9040 is used to measure the pH of aqueous wastes and those multiphase wastes where the aqueous phase constitutes at least 20% of the total volume of the waste.

1.2 The corrosivity of concentrated acids and bases, or of concentrated acids and bases mixed with inert substances, cannot be measured. The pH measurement requires some water content.

2.0 SUMMARY

2.1 The pH of the sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. The measuring device is calibrated using a series of standard solutions of known pH.

3.0 INTERFERENCES

3.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or moderate (< 0.1 molar solution) salinity.

3.2 Sodium error at H levels > 10 can be reduced or eliminated by using a low-sodium-error electrode.

3.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by rinsing with distilled water. An additional treatment with hydrochloric acid (1:10) may be necessary to remove any remaining film.

3.4 Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference should be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. This error is sample-dependent and cannot be controlled. It should, therefore, be noted by reporting both the pH and temperature at the time of analysis.

4.0 APPARATUS AND MATERIALS

4.1 pH meter: Laboratory or field model. Many instruments are commercially available with various specifications and optional equipment.

4.2 Glass electrode.

4.3 Reference electrode: A silver-silver chloride or other reference electrode of constant potential may be used.

> NOTE: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

4.4 Magnetic stirrer and Teflon-coated stirring bar.

4.5 Thermometer and/or temperature sensor for automatic compensation.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Primary standard buffer salts are available from the National Institute of Standards and Technology (NIST) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.3 Secondary standard buffers may be prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions have been validated by comparison with NIST standards and are recommended for routine use.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples musts be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 **PROCEDURE**

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. (For corrosivity characterization, the calibration of the pH meter should include a buffer of pH 2 for acidic wastes and a pH 12 buffer for caustic wastes; also, for corrosivity characterization, the sample must be measured at 25±1°C if the pH of the waste is above 12.0.) Various instrument designs may involve use of a dial (to "balance" or "standardize") or a slope adjustment, as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar. If field measurements are being made, the electrodes may be immersed directly into the sample stream to an adequate depth and moved in a manner to ensure sufficient sample movement across the electrode-sensing element as indicated by drift-free readings (< 0.1 pH).

7.3 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

7.4 Thoroughly rinse and gently wipe the electrodes prior to measuring pH of samples. Immerse the electrodes into the sample beaker or sample stream and gently stir at a constant rate to provide homogeneity and suspension of solids. Note and record sample pH and temperature. Repeat measurement on successive aliquots of sample until values differ by < 0.1 pH units. Two or three volume changes are usually sufficient.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for the appropriate QC protocols.

8.2 Electrodes musts be thoroughly rinsed between samples.

9.0 METHOD PERFORMANCE

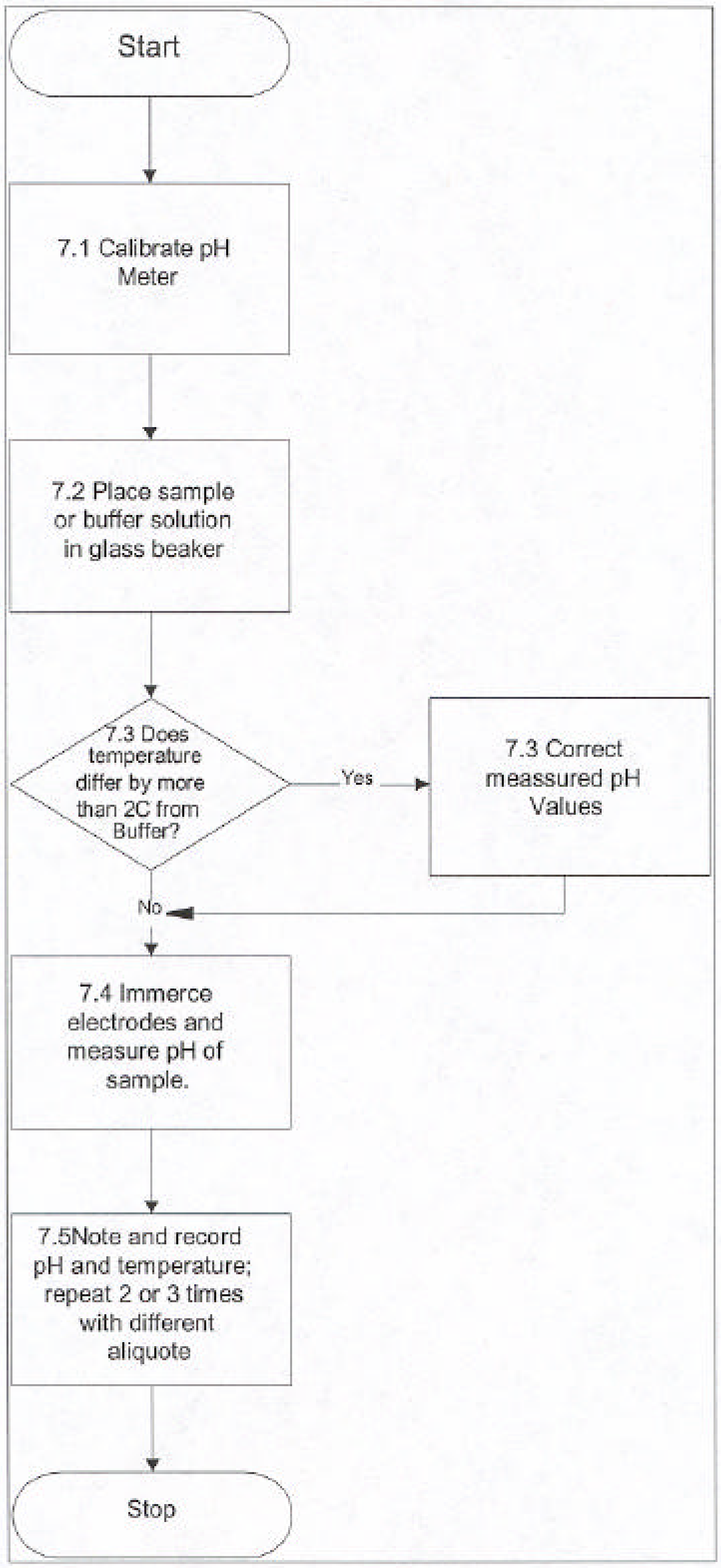
9.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

		Accuracy as	
	Standard Deviation	Bias	Bias
pH Units	pH Units	%	pH Unit
3.5	0.10	-01.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+ 1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

10.0 REFERENCES

1. National Bureau of Standards, Standard Reference Material Catalog 1986-87, Special Publication 260.

METHOD 9040B
pH ELECTROMETRIC MEASUREMENT



3. C.2 METHOD 9045C

SOIL AND WASTE pH

1.0 SCOPE AND APPLICATION

1.1 Method 9045 is an electrometric procedure for measuring pH in soils and waste samples. Wastes may be solids, sludges, or non-aqueous liquids. If water is present, it must constitute less than 20 % of the total volume of the sample.

2.0 SUMMARY OF METHOD

2.1 The sample is mixed with reagent water, and the pH of the resulting aqueous solution is measured.

3.0 INTERFERENCES

3.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of > 10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of < 1, may give incorrectly high pH measurements.

3.2 Temperature fluctuations will cause measurement errors.

3.3 Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can (1) be cleaned with an ultrasonic bath, or (2) be washed with detergent, rinsed several times with water, placed in 1:10 HC 1 so that the lower third of the electrode is submerged, and then thoroughly rinsed with water, or (3) be cleaned per the manufacturer's instructions.

4.0 APPARATUS AND MATERIALS

4.1 pH Meter with means for temperature compensation.

4.2 Glass Electrode.

4.3 Reference electrode: A silver-silver chloride or other reference electrode of constant potential may be used.

> NOTE: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

4.4 Beaker: 50-mL.

4.5 Thermometer and/or temperature sensor for automatic compensation.

4.6 Analytical balance: capable of weighing 0.1 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Primary standard buffer salts are available from the National Institute of Standards and Technology (NIST) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.4 Secondary standard buffers may be prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions, which have been validated by comparison with NIST standards, are recommended for routine use.

6.0 SAMPLE PRESERVATION AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

Appendix Three - Analyses for the Corrosivity Characteristic - Method 9045C

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value. If an accurate pH reading based on the conventional pH scale [0 to 14 at 25°C] is required, the analyst should control sample temperature at 25±1°C when sample pH approaches the alkaline end of the scale (e.g., a pH of 11 or above).

7.2 Sample preparation and pH measurement of soils:

7.2.1 To 20 g of soil in a 50-mL beaker, add 20 mL of reagent water, cover, and continuously stir the suspension for 5 minutes. Additional dilutions are allowed if working with hygroscopic soils and salts or other problematic matrices.

7.2.2 Let the soil suspension stand for about 1 hour to allow most of the suspended clay to settle out from the suspension or filter or centrifuge off the aqueous phase for pH measurement.

7.2.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrodes into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.2.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values musts be corrected.

7.2.5 Report the results as "soil pH measured in water at __°C" where " __°C" is the temperature at which the test was conducted.

7.3 Sample preparation and pH measurement of waste materials:

7.3.1 To 20 g of waste sample in a 50-mL beaker, add 20 mL of reagent water, cover, and continuously stir the suspension for 5 minutes. Additional dilutions are allowed if working with hygroscopic wastes and salts or other problematic matrices.

7.3.2 Let the waste suspension stand for about 15 minutes to allow most of the suspended waste to settle out from the suspension or filter or centrifuge off aqueous phase for pH measurement.

NOTE: If the waste is hygroscopic and absorbs all the reagent water, begin the experiment again using 20 g of waste and 40 mL of reagent water.

NOTE: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned (Step 3.3) if it becomes coated with an oily material.

7.3.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant to establish good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrode into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.3.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.3.5 Report the results as "waste pH measured in water at _°C" where " °C" is the temperature at which the test was conducted.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for the appropriate QC protocols.
8.2 Electrodes must be thoroughly rinsed between samples.

9.0 METHOD PERFORMANCE

9.1 No data provided.

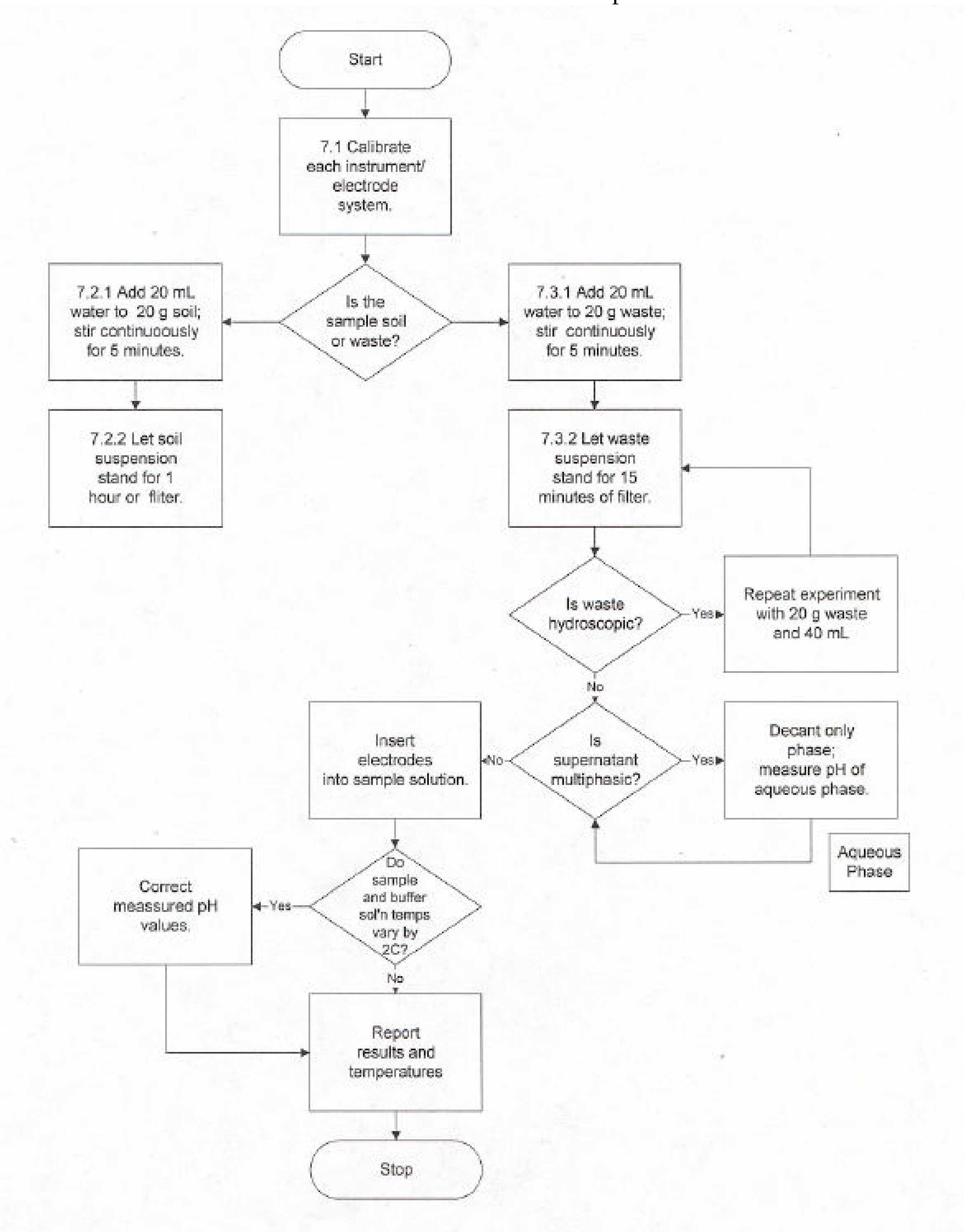
10.0 REFERENCES

1. Black, Charles Allen; Methods of Soil Analysis; American Society of Agronomy: Madison, WI, 1973.
2. National Bureau of Standards, Standard Reference Material Catalog, 1986-87, Special Publication 260.

Appendix Three - Analyses for the Corrosivity Characteristic - Method 9045C

METHOD 9045C

SOIL AND WASTE pH



3.C.3 METHOD 1110

CORROSIVITY TOWARD STEEL

1.0 SCOPE AND APPLICATION

1.1 Method 1110 is used to measure the corrosivity toward steel of both aqueous and nonaqueous liquid wastes.

2.0 SUMMARY OF METHOD

2.1 This test exposes coupons of SAE Type 1020 steel to the liquid waste to be evaluated and, by measuring the degree to which the coupon has been dissolved, determines the corrosivity of the waste.

3.0 INTERFERENCES

3.1 In laboratory tests, such as this one, corrosion of duplicate coupons is usually reproducible to within 10 percent. However, large differences in corrosion rates may occasionally occur under conditions where the metal surfaces become passivated. Therefore, at least duplicate determinations of corrosion rate should be made.

4.0 APPARATUS AND MATERIALS

4.1 An apparatus should be used, consisting of a kettle or flask of suitable size (usually 500 to 5,000 mL, a reflux condenser, a thermowell and temperature regulating device, a heating device (mantle, hot plate, or bath), and a specimen support system. A typical resin flask set up for this type of test is shown in Figure 1.

4.2 The supporting device and container shall be constructed of materials that are not affected by, or cause contamination of, the waste under test.

4.3 The method of supporting the coupons will vary with the apparatus used for conducting the test, but it should be designed to insulate the coupons from each other physically and electrically and to insulate the coupons from any metallic container or other device used in the test. Some common support materials include glass, fluorocarbon, or coated metal.

4.4 The shape and form of the coupon support should ensure free contact with the waste.

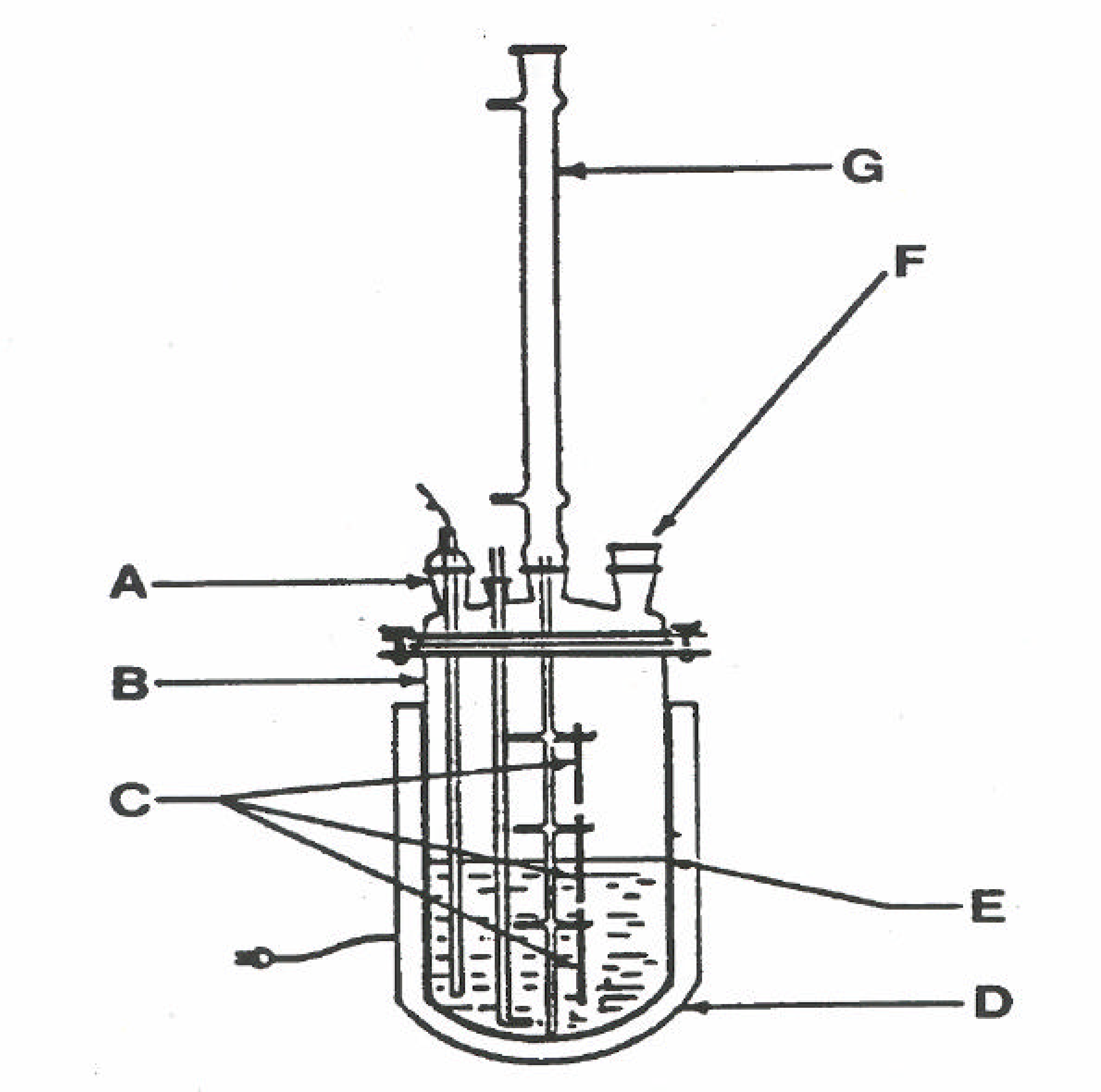


Figure 1. Typical resin flask that can be used as a versatile and convenient apparatus to conduct simple immersion tests. Configuration of the flask top is such that more sophisticated apparatus can be added as required by the specific test being conducted. A = thermowell, B = resin flask, C = specimens hung on supporting device, D = heating mantle, E = liquid interface, F = opening in flask for additional apparatus that may be required, and G = reflux condenser.

4.5 A circular specimen of SAE 1020 steel of about 3.75 cm (1.5 in.) diameter is a convenient shape for a coupon. With a thickness of approximately 0.32 cm (0.125 in.) and a 0.80-cm (0.4-in.)-diameter hole for mounting, these specimens will readily pass through a 45/50 ground-glass joint of a distillation kettle. The total surface area of a circular specimen is given by the following equation:

$$A = 3.14/2(D^2-d^2) + (t)(3.14)(D) + (t)(3.14)(d)$$

where:

t = thickness.
D = diameter of the specimen.
d = diameter of the mounting hole.

If the hole is completely covered by the mounting support, the last term in the equation, (t)(3.14)(d), is omitted.

4.5.1 All coupons should be measured carefully to permit accurate calculation of the exposed areas. An area calculation accurate to ±1 percent is usually adequate.

4.5.2 More uniform results may be expected if a substantial layer of metal is removed from the coupons prior to testing the corrosivity of the waste. This can be accomplished by chemical treatment (pickling), by electrolytic removal, or by grinding with a coarse abrasive. At least 0.254 mm (0.0001 in.) or 2-3 mg/cm2 should be removed. Final surface treatment should include finishing with #120 abrasive paper or cloth. Final cleaning consists of scrubbing with bleach-free scouring powder, followed by rinsing in distilled water and then in acetone or methanol, and finally by air-drying. After final cleaning, the coupon should be stored in a desiccator until used.

4.5.3 The minimum ratio of volume of waste to area of the metal coupon to be used in this test is 40 mL/cm2.

5.0 REAGENTS

5.1 Sodium hydroxide (NaOH), (20 percent): Dissolves 200 g NaOH in 800 mL Type II water and mix well.

5.2 Zinc dust.

5.3 Hydrochloric acid (HC1): Concentrated.

5.4 Stannous chloride ($SnC1_2$).

5.5 Antimony chloride ($SbC1_3$).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples should be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

7.0 PROCEDURE i

7.1 Assemble the test apparatus as described in Paragraph 4.0, above.

7.2 Fill the container with the appropriate amount of waste.

7.3 Begin agitation at a rate sufficient to ensure that the liquid is kept well mixed and homogeneous.

7.4 Using the heating device, bring the temperature of the waste to 55 degrees C (130 degrees F).

7.5 An accurate rate of corrosion is not required; only a determination as to whether the rate of corrosion is less than or greater than 6.35 mm per year is required. A 24 hr test period should be ample to determine whether or not the rate of corrosion is > 6.35 mm per year.

7.6 In order to determine accurately the amount of material lost to corrosion, the coupons have to be cleaned after immersion and prior to weighing. The cleaning procedure should remove all products of corrosion while removing a minimum of sound metal. Cleaning methods can be divided into three general categories: mechanical, chemical, and electrolytic.

7.6.1 Mechanical cleaning includes scrubbing, scraping, brushing, and ultrasonic procedures. Scrubbing with a bristle brush and mild abrasive is the most popular of these methods. The others are used in cases of heavy corrosion as a first step in removing heavily encrusted corrosion products prior to scrubbing. Care should be taken to avoid removing sound metal.

7.6.2 Chemical cleaning implies the removal of material from the surface of the coupon by dissolution in an appropriate solvent. Solvents such as acetone, dichloromethane, and alcohol are used to remove oil, grease, or resinous materials and are used prior to immersion to remove the products of corrosion. Solutions suitable for removing corrosion from the steel coupon are:

Solution	Soaking Time	Temperature
20 % NaOH + 200 g/L zinc dust	5 min	Boiling
or		

Conc. HC l + 50 g/L $SnC1_2$ + 20 g/L $SbC1_3$	Until clean	Cold

7.6.3 Electrolytic cleaning should be preceded by scrubbing to remove loosely adhering corrosion products. One method of electrolytic cleaning that can be employed uses:

Solution:	50 g/L H_2S0_4
Anode:	Carbon or lead
Cathode:	Steel coupon
Cathode current density:	20 amp/cm^2 (129 amp/$in.^2$)
Inhibitor:	2 cc organic inhibitor/liter
Temperature:	74 degrees C (165 degrees F)
Exposure Period:	3 min.

NOTE: Precautions must be taken to ensure good electrical contact with the coupon to avoid contamination of the cleaning solution with easily reducible metal ions and to ensure that inhibitor decomposition has not occurred. Instead of a proprietary inhibitor, -0.5 g/L of either diorthotolyl thiourea of quinolin ethiodide can be used.

7.7 Whatever treatment is employed to clean the coupons, its effect in removing sound metal should be determined by using a blank (i.e., a coupon that has not been exposed to the waste). The blank should be cleaned along with the test coupon and its waste loss subtracted from that calculated for the test coupons.

7.8 After corroded specimens have been cleaned and dried, they are reweighted. The weight loss is employed as the principal measure of corrosion. Use of weight loss as a measure of corrosion requires making the assumption that all weight loss has been due to generalized corrosion and not localized pitting. In order to determine the corrosion rate for the purpose of this regulation, the following formula is used:

$$\text{Corrosion Rate (mmpy)} = \frac{\text{weight loss x 11.145}}{\text{area x time}}$$

where: weight loss is in milligrams,
area in square centimeters,
time in hours, and
corrosion rate in millimeters per year (mmpy).

8.0 QUALITY CONTROL

8.1 All quality control data should be filed and available for auditing.

8.2 Duplicate samples should be analyzed on a routine basis.

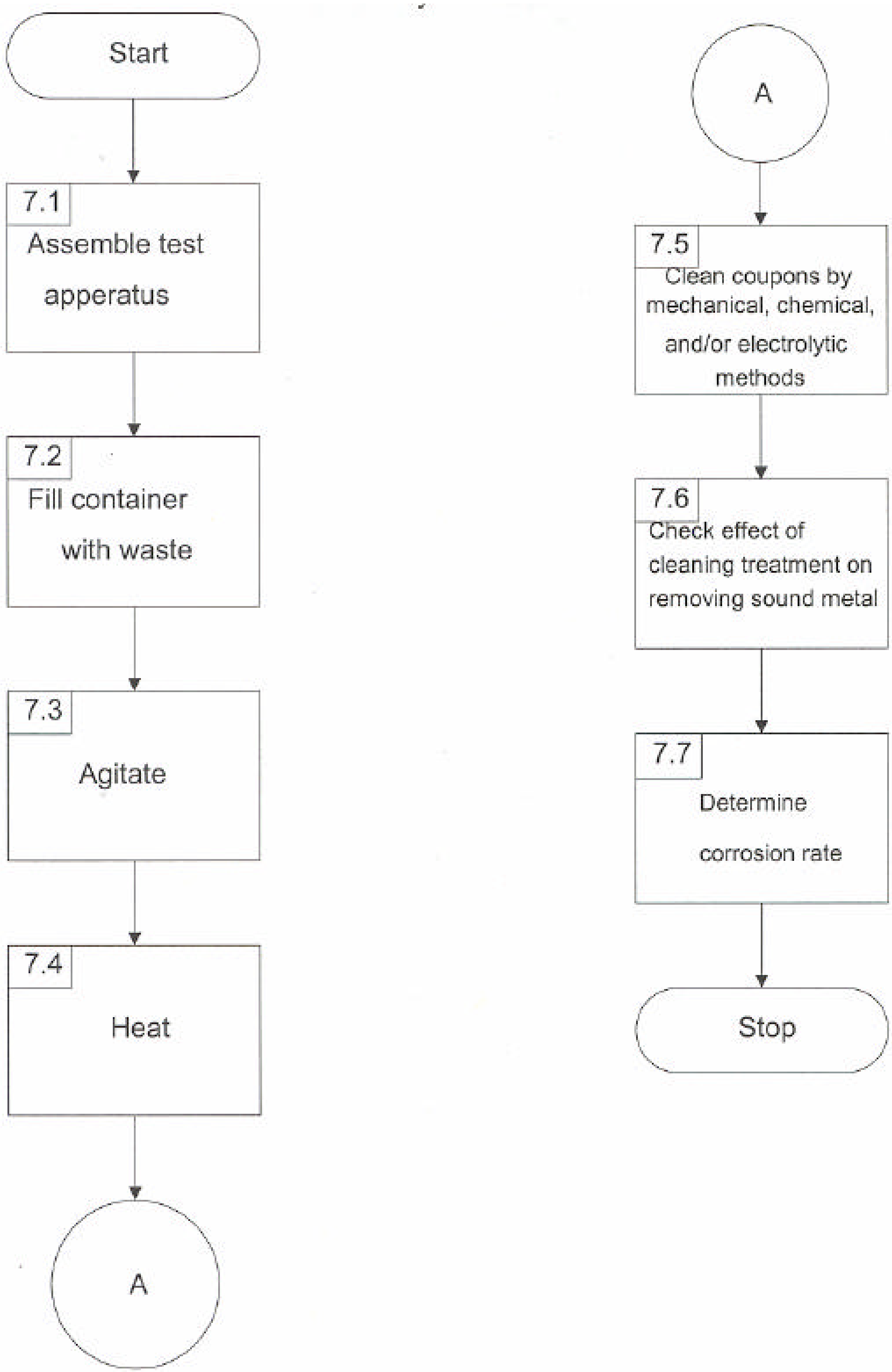
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. National Association of Corrosion Engineers, "Laboratory Corrosion Testing of Metals for the Process Industries," NACE Standard TM-01-69 (1972 Revision), NACE, 3400 West Loop South, Houston, TX 77027.

Method 1110
Corrosivity Toward Steel



3. D.1 METHOD 7.3.3.2

TEST METHOD TO DETERMINE HYDROGEN CYANIDE RELEASED FROM WASTES 1

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to all wastes, with the condition that wastes that are combined with acids do not form explosive mixtures.

1.2 This method provides a way to determine the specific rate of release of hydrocyanic acid upon contact with an aqueous acid.

1.3 This test measures only the hydrocyanic acid evolved at the test conditions. It is not intended to measure forms of cyanide other than those that are evolvable under the test conditions.

2.0 SUMMARY OF METHOD

2.1 An aliquot of acid is added to a fixed weight of waste in a closed system. The generated gas is swept into a scrubber. The analyte is quantitated. The procedure for quantitating the cyanide is Method 9014.

3.0 INTERFERENCES

3.1 Interferences are undetermined.

4.0 APPARATUS AND MATERIALS (See Figure 1)

4.1 Round-bottom flask - 500-mL, three-neck, with 24/40 ground-glass joints.

4.2 Gas scrubber - 50 mL calibrated scrubber

4.3 Stirring apparatus - To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination or an overhead motor-driven propeller stirrer.

4.4 Addition funnel - With pressure-equalizing tube and 24/40 ground-glass joint and Teflon sleeve. '

4.5 Flexible tubing - For connection from nitrogen supply to apparatus.

4.6 Water-pumped or oil-pumped nitrogen gas - With two-stage regulator.

4.7 Rotometer - For monitoring nitrogen gas flow rate.

4.8 Analytical balance - capable of weighing to 0.001 g.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sulfuric acid (O.O1N), HZS04. Add 2.8 mL concentrated H2S04to organic-free reagent water and dilute to 1 L. Withdraw 100 mL of this solution and dilute to 1 L to make the O.O1N HZS04;

5.4 Cyanide reference solution, (1000 mg/L). Dissolve approximately 2.5 g of KOH and 2.51 g of KCN in 1 liter of organic-free reagent water. Standardize with 0.0192N AgN03' Cyanide concentration in this solution should be 1 mg/mL.

5.5 Sodium hydroxide solution (1.25, NaOH. Dissolve 50 g of NaOH in reagent water and dilute to 1 liter with organic-free reagent water.

5.6 Sodium hydroxide solution (0.25N,, NaOH. Dilute 200 mL of 1.25N sodium hydroxide solution (Step 5.5) to 1 liter with organic-free reagent water.

5.7 Silver nitrate solution (0.0192N,. Prepare by crushing approximately 5 g of AgN03 crystals and drying to constant weight at 40°C. Weigh 3.265 g of dried AgN031. dissolve in organic-free reagent water, and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Samples containing, or suspected of containing, sulfide or a combination of sulfide and cyanide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should commence as soon as possible, and samples should be kept in a cool, dark place until analysis begins.

6.2 It is suggested that samples of cyanide wastes be tested as quickly as possible. Although they can be preserved by adjusting the sample pH to 12 with strong base, this will cause dilution of the sample, increase the ionic strength, and, possibly, change other physical or chemical characteristics of the waste which may affect the rate of release of the hydrocyanic acid. Storage of samples should be under refrigeration and in the dark.

6.3 Testing should be performed in a ventilated hood.

7.0 PROCEDURE

7.1 Add 50 mL of 0.25N NaOH solution (Step 5.6) to a calibrated scrubber and dilute with organic-free reagent water to obtain an adequate depth of liquid.

7.2 Close the system and adjust the flow rate of nitrogen, using the rotometer. Flow should be 60 mL/min.

7.3 Add 10 g of the waste to be tested to the system.

7.4 With the nitrogen flowing, add enough sulfuric acid to fill the flask half full. Start the 30 minute test period.

7.5 Begin stirring while the acid is entering the round-bottom flask. The stirring speed must remain constant throughout the test.

NOTE: The stirring should not be fast enough to create a vortex.

7.6 After 30 minutes, close off the nitrogen and disconnect the scrubber. Determine the amount of cyanide in the scrubber by Method 9014.

NOTE: Delete the "C" and "D" terms from the spectrophotometric procedure calculation and the "E" and "F" terms from the titration procedure calculation in Method 9014. These terms are not necessary for the reactivity determination because the terms determine the amount of cyanide in the entire sample, rather than only in the aliquot taken for analysis.

8.0 CALCULATIONS

8.1 Determine the specific rate of release of HCN, using the following parameters:

X = Concentration of HCN in diluted scrubber solution (mg/L)
(This is obtained from Method 9014.)

L = Volume of solution in scrubber (L)

W = Weight of waste used (kg)

S = Time of measurement (sec.) = Time N_2 stopped - Time N_2 started

R = specific rate of release (mg/kg/sec.) = $\frac{X ? L}{W ? S}$

Total releasable HCN (mg/kg) = R x S

9.0 METHOD PERFORMANCE

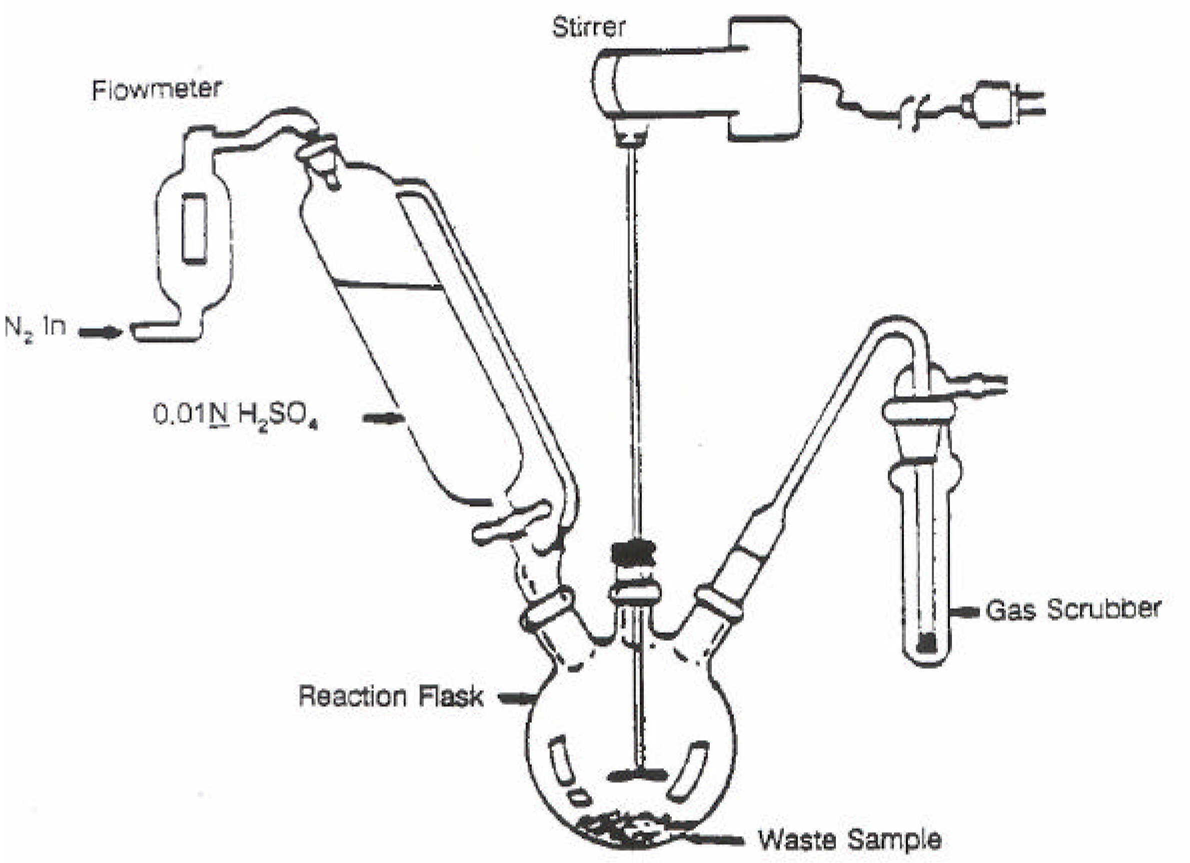
9.1 The operation of the system can be checked and verified using the cyanide reference solution (Step 5.4). Perform the procedure using the reference solution as a sample and determine the percent recovery. Evaluate the standard recovery based on historical laboratory data, as stated in Chapter One.

10.0 REFERENCES

10.1 No references are available at this time.

FIGURE 1.

APPARATUS TO DETERMINE HYDROGEN CYANIDE RELEASED FROM WASTES



3.D.2 METHOD 7.3.4.2

<u>TEST METHOD TO DETERMINE HYDROGEN SULFIDE RELEASED FROM WASTES</u>

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to all wastes, with the condition that wastes that are combined with acids do not form explosive mixtures.

1.2 This method provides a way to determine the specific rate of release of hydrogen sulfide upon contact with an aqueous acid.

1.3 This procedure releases only the hydrogen sulfide evolved at the test conditions. It is not intended to measure forms of sulfide other than those that are evolvable under the test conditions.

2.0 SUMMARY OF METHOD

2.1 An aliquot of acid is added to a fixed weight of waste in a closed system. The generated gas is swept into a scrubber. The analyte is quantified. The procedure for quantifying the sulfide is given in Method 9034.

3 .0 INTERFERENCES

3.1 Interferences are undetermined.

4.0 APPARATUS AND MATERIALS (See Figure 2)

4.1 Round-bottom flask - 500-mL, three-neck, with 24/40 ground-glass joints.

4.2 Gas scrubber - 50 mL calibrated scrubber.

4.3 Stirring apparatus - To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination or an overhead motor-driven propeller stirrer.

4.4 Addition funnel - With pressure-equalizing tube and 24/40 ground-glass joint and Teflon sleeve.

4.5 Flexible tubing - For connection from nitrogen supply to apparatus.

4.6 Water-pumped or oil-pumped nitrogen gas - With two-stage regulator.

4.7 Rotometer - For monitoring nitrogen gas flow rate.

4.8 Analytical balance - capable of weighing to 0.001 g.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sulfuric acid (O.O1N), H_2S0_4. Add 2.8 mL concentrated H_2S0_4 to organic-free reagent water and dilute to 1 L. Withdraw 100 mL of this solution and dilute to 1 L to make the O.O1N H_2S0_4.

5.4 Sulfide reference solution - Dissolve 4.02 g of $Na_2S \cdot 9H_20$ in 1.0 L of organic-free reagent water. This solution contains 570 mg/L hydrogen sulfide. Dilute this stock solution to cover the analytical range required (100-570 mg/L).

5.5 Sodium hydroxide solution (0.25N), NaOH. Dissolve 50 g of NaOH in organic-free reagent water and dilute to 1 L with organic-free reagent water.

5.6 Sodium hydroxide solution (0.25N), NaOH. Dilute 200 ml, of 1.25N sodium hydroxide solution (Step 5.5) to 1 L with organic-free reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Samples containing, or suspected of containing, sulfide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should commence as soon as possible, and samples should be kept in a cool, dark place until analysis begins.

6.2 It is suggested that samples of sulfide wastes be tested as quickly as possible. Although they can be preserved by adjusting the sample pH to 12 with strong base and adding zinc acetate to the sample, these will cause dilution of the sample, increase the ionic strength, and, possibly, change other physical or chemical characteristics of the waste which may affect the rate of release of the hydrogen sulfide. Storage of samples should be under refrigeration and in the dark. '"

6.3 Testing should be performed in a ventilated hood.

7.0 PROCEDURE

7.1 Add 50 mL of 0.25N NaOH solution to a calibrated scrubber and dilute with organic-free reagent water to obtain an adequate depth of liquid.

7.2 Assemble the system and adjust the flow rate of nitrogen, using the rotometer. Flow should be 60 mL/min.

7.3 Add 10 g of the waste to be tested to the system.

7.4 With the nitrogen flowing, add enough sulfuric acid to fill the flask half full, while starting the 30 minute test period.

7.5 Begin stirring while the acid is entering the round-bottom flask. The stirring speed must remain constant throughout the test.

NOTE: The stirring should not be fast enough to create a vortex.

7.6 After 30 minutes, close off the nitrogen and disconnect the scrubber. Determine the amount of sulfide in the scrubber by Method 9034.

7.7 Substitute the following for Step p7.3.2 in Method 9034: The trapping solution must be brought to a pH of 2 before proceeding. Titrate a small aliquot of the trapping solution to a pH 2 end point with 6N HCI and calculate the amount of HCI needed to acidify the entire scrubber solution. Combine the small acidified aliquot with the remainder of the acidified scrubber solution.

8.0 CALCULATIONS

8.1 Determine the specific rate of release of HZS, using the following parameters:

X = Concentration of H2S in scrubber (mg/L). (This is obtained from Method 9034.)

L = Volume of solution in scrubber (L)

W = Weight of waste used (kg)

S = time of experiment (sec.) = Time NZ stopped - Time NZ started

R = specific rate of release (mg/kg/sec.) = $\dfrac{X ? L}{W ? S}$

Total releasable H_2S (mg/kg) = R x S

9.0 METHOD PERFORMANCE

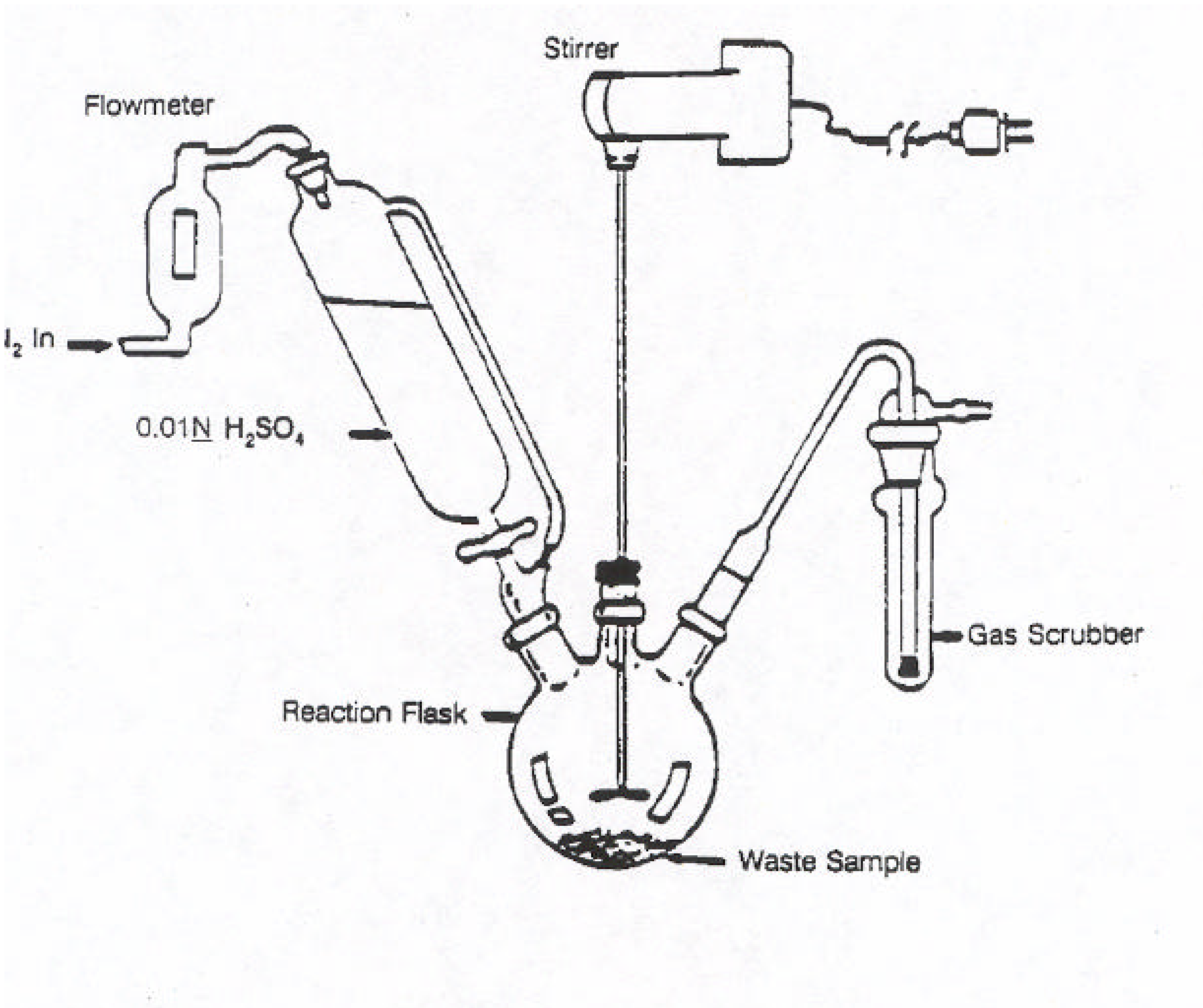
9.1 The operation of the system can be checked and verified using the sulfide reference solution (Step 5.4). Perform the procedure using the reference solution as a sample and determine the percent recovery. Evaluate the standard recovery based on historical laboratory data, as stated in Chapter One.

10.0 REFERENCES

10.1 No references are available at this time.

FIGURE 2.

APPARATUS TO DETERMINE HYDROGEN SULFIDE RELEASED FROM WASTES



3.D.3 METHOD 9014

TITRIMETRIC AND MANUAL SPECTROPHOTOMETRIC DETERMINATIVE METHODS FOR CYANIDE

1.0 SCOPE AND APPLICATION

1.1 This method can be used for measuring free (non-complexed) cyanide and hydrocyanic acid in drinking water, natural surface waters, domestic and industrial wastewater, and in soil extracts. This method may also be used as a determinative step for quantifying total and amenable cyanide in the alkaline distillates from Method 9010.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 0.1 mg/L (0.025 mg/250 mL of absorbing liquid):

1.3 The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

2.0 SUMMARY OF METHOD

2.1 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCI) by reaction of cyanide with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 578 nm for the complex formed with pyridine-barbituric acid reagent and CNCI. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.2 The titration measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure provided in Method 9010.

Refer to Method 9010 for a discussion of potential cyanide interferences.

4.0 APPARATUS AND MATERIALS

4.1 Spectrophotometer - Suitable for measurements at 578 nm with a 1.0 cm cell or larger.

4.2 Hot plate stirrer/hearing mantle.

4.3 pH meter.

4.4 Refrigerator.

4.5 5 ml, microburette.

4.6 Class A volumetric flasks - 1000, 250, and 100 mL.

4.7 Erlenmeyer flask - 500 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it , is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Reagents for spectrophotometric determination

5.3.1 Sodium hydroxide solution (0.25N), NaOH. Dissolve 10 g NaOH in 1 liter of water.

5.3.2 Sodium phosphate monobasic (1M), NaH_2P0_4? H_20. Dissolve 138 g of NaH_2P0_4?H_20 in 1 liter of water. Refrigerate this solution.

5.3.3 Chloramine-T solution (0.44%), $C_7H_7CINNaO_2S$. Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of water and refrigerate until ready to use.

5.3.4 Pyridine-Barbituric acid reagent, C_5H_5N ? $C_4H_4N_20_3$. Place 15 g of barbituric acid in a 250-ml, volumetric flask and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 ml, of pyridine and mix. Add 15 mL of concentrated hydrochloric acid (HCI), mix, and cool to room temperature. Dilute to 250 mL with water. This reagent is stable for approximately six months if stored in a cool, dark place.

5.3.5 Stock potassium cyanide solution (1 mL = 1000 µg CN), KCN. Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of water. Standardize with 0.0192N silver nitrate, AgN03. Dilute to appropriate concentration to achieve 1 mL = 1000 µg of CN.

NOTE: Detailed procedure for AgN03 standardization is described in "Standard Methods for the Examinatio n of Water and Wastewater," 18th Edition, (1992), Methods 4500-CN D.

5.3.6 Intermediate standard potassium cyanide solution, (1 mL = 100 µg CN), KCN. Dilute 100 mL of stock potassium cyanide solution (1 mL = 1000 µg CN) to 1000 mL with water.

5.3.7 Working standard potassium cyanide solution, (1 mL = 10 pg CN), KCN. Prepare fresh daily by diluting 100 ml, of intermediate standard potassium cyanide solution and 10 mL of 1N NaOH to 1 liter with water:

5.4 Reagents for titration procedure

5.4.1 Rhodanine indicator - Dissolve 20 mg of p-dimethylamino-benzal-rhodanine, $C_{12}H_{12}N_2OS_2$, in 100 mL of acetone.

5.4.2 Standard silver nitrate solution (0.0192N), AgN03. Prepare by crushing approximately 5 g $AgN0_3$ and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgN0_3$. Dissolve in 1 liter of water.

NOTE: Detailed procedure for $AgN0_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater," 18th Edition, (1992), Method 4500-CN D.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 9010 for guidance on sample collection, preservation, and handling.

6.2 Distillates that are not analyzed immediately should be stored in tightly sealed flasks at 4°C.

7.0 PROCEDURE

7.1 If the manual spectrophotometric determination will be performed, proceed to Section 7.2. If the titration procedure will be performed, proceed to Section 7.6.

7.2 Manual spectrophotometric determination

7.2.1 Pipet 50 mL of sample or 50 mL of the scrubber solution obtained from the distillation procedure in Method 9010 into a 100-mL volumetric flask. If the sample is later found to be beyond the linear range of the colorimetric determination and redistillation of a smaller sample is not feasible, a smaller aliquot may be taken. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution.

NOTE: Temperature of reagents and spiking solution can affect the response factor of the colorimetric determination. The reagents stored in the refrigerator should be warmed to ambient temperature before use. Samples should not be left in a warm instrument to develop color, but instead they should be aliquoted to a cuvette immediately prior to reading the absorbance.

7.2.2 Add 15 mL of 1M sodium phosphate solution and mix. Add 2 mL of chloramine-T and mix. Some distillates may contain compounds that have chlorine demand. One minute after the addition of chloramine-T, test for excess chlorine with KI-starch paper. If the test is negative, add 0.5 mL chloramine-T. After one minute recheck with KI-starch paper. Continue to add chloramine-T in 0.5 mL increments until an excess is maintained. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution and mix.

7.2.3 Dilute to 100 mL with water and mix again. Allow 8 minutes for color development and then read the absorbance at 578 nm in a 1-cm cell within 15 minutes. The sodium hydroxide concentration will be 0.125N.

7.3 Standard curve for samples without sulfide

7.3.1 Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25N sodium hydroxide and dilute to 250 mL with water. Prepare using the following table. The sodium hydroxide concentration will be 0.25N.

mL of Working Standard Solution (1 mL = 10 µg CN)	Concentration (µg CN/L)
0	Blank
1.0	40
2.0	80
5.0	200
10.0	400
15.0	600
20.0	800

7.3.2 After the standard solutions have been prepared according to the table above, pipet 50 mL of each standard solution into a 100-mL volumetric flask and

Chemical Testing Methods for Designating Dangerous Waste

proceed to Sections 7.2.2 and 7.2.3 to obtain absorbance values for the standard curve. ', The final concentrations for the standard curve will be one half of the amounts in the above table (final concentrations ranging from 20 to 400 µg/L.

7.3.3 Prepare a standard curve ranging from 20 to 400 µg/L by plotting absorbance of standard versus the cyanide concentration.

7.4 Standard curve for samples with sulfide

7.4.1 It is imperative that all standards be distilled in the same manner as the' samples using the method of standard additions. Standards distilled by this method will give a linear curve, at low concentrations, but as the concentration increases, the recovery decreases. It is recommended that at least five standards be distilled.

7.4.2 Prepare a series of standards similar in concentration to those mentioned ' in Section 7.3.1 and analyze as in Section 7.2. Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration.

7.5 Calculation - If the spectophotometric procedure is used, calculate the cyanide, in µg/L, in the original sample as follows.

$$CN\ (\mu g/L) = \frac{AxBxC}{DxE}$$

where:

Å = µg/L CN read from standard curve.
B = ml, of sample after preparation of colorimetric analysis (100 mL recommended).
C = mL of sample after distillation (250 ml, recommended).
D = mL of original sample for distillation (500 mL recommended.)
E = mL used for colorimetric analysis (50 ml, recommended).

7.6 Titration Procedure

7.6.1 Transfer the gas scrubber solution or a suitable aliquot from the 250-mL volumetric flask to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator.

7.6.2 Titrate with standard 0.0192N silver nitrate to the first change in color from yellow to brownish-pink. The titration must be performed slowly with constant stirring. Titrate a water blank using the same amount of sodium hydroxide and indicator as in the sample. The analyst should be familiar with the endpoint of the titration and the amount of indicator to be used before actually titrating the samples. A 5-ml, buret may be conveniently used to obtain a precise titration:

NOTE: The titration is based on the following reaction:

Ag^{+} + 2CN ? {Ag(CN)$_2$]

When all of the cyanide has complexed and more silver nitrate is added, the excess silver combines with the rhodanine indicator to turn the solution yellow and then brownish-pink.

7.6.3 Calculation - If the titrimetric procedure is used, calculate concentration of CN- in µg/L in the original sample as follows:

$$CN\text{-}(\mu g/L) = \frac{(A - B)}{C} \times D \times \frac{E}{F} \times \frac{2\ mole\ CN^{-}}{1\ eq.\ 4gNO_3} \times \frac{26.02\ g\ CN^{-}}{1\ mole\ CN^{-}} \times \frac{1 \times 10^{6}\ \mu g}{1\ g}$$

where:

A = ml, of $AgN0^{3}$ for titration of sample.
B = ml, of $AgN0_3$ for titration of blank.
C = ml, of sample titrated (250 recommended).
D =actual normality of $AgN0_3$ (0.0192N recommended).
E = mL of sample after distillation (250 recommended).
F = mL of original sample before distillation (500 recommended).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Refer to the quality control section of Method 9010A for the method requirements for blanks, matrix duplicates, and matrix spikes. Each QC sample must be processed through the reflux-distillation steps contained in Method 9010 prior to analysis by this method.

8.3 Analyze check standards with every analytical batch of samples. If the standards are not within 15% of the expected value, then the samples must be reanalyzed.

8.4 Analyze one replicate sample for every 20 samples. The CV of the replicates should be 20% or less. If this criterion is not met, the samples should be reanalyzed.

8.5 Analyze one matrix spiked sample every 20 samples to check the efficiency of sample distillation procedure and to monitor potential matrix interference.

8.6 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

9.0 METHOD PERFORMANCE

9.1 The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

9.2 EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.06 to 0.62 mg/L CN-, the standard deviations for precision were ± 0.005 to t 0.094, respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0. 62 mg/L CN-, recoveries (accuracy) were 85 % and 102 % ,respectively.

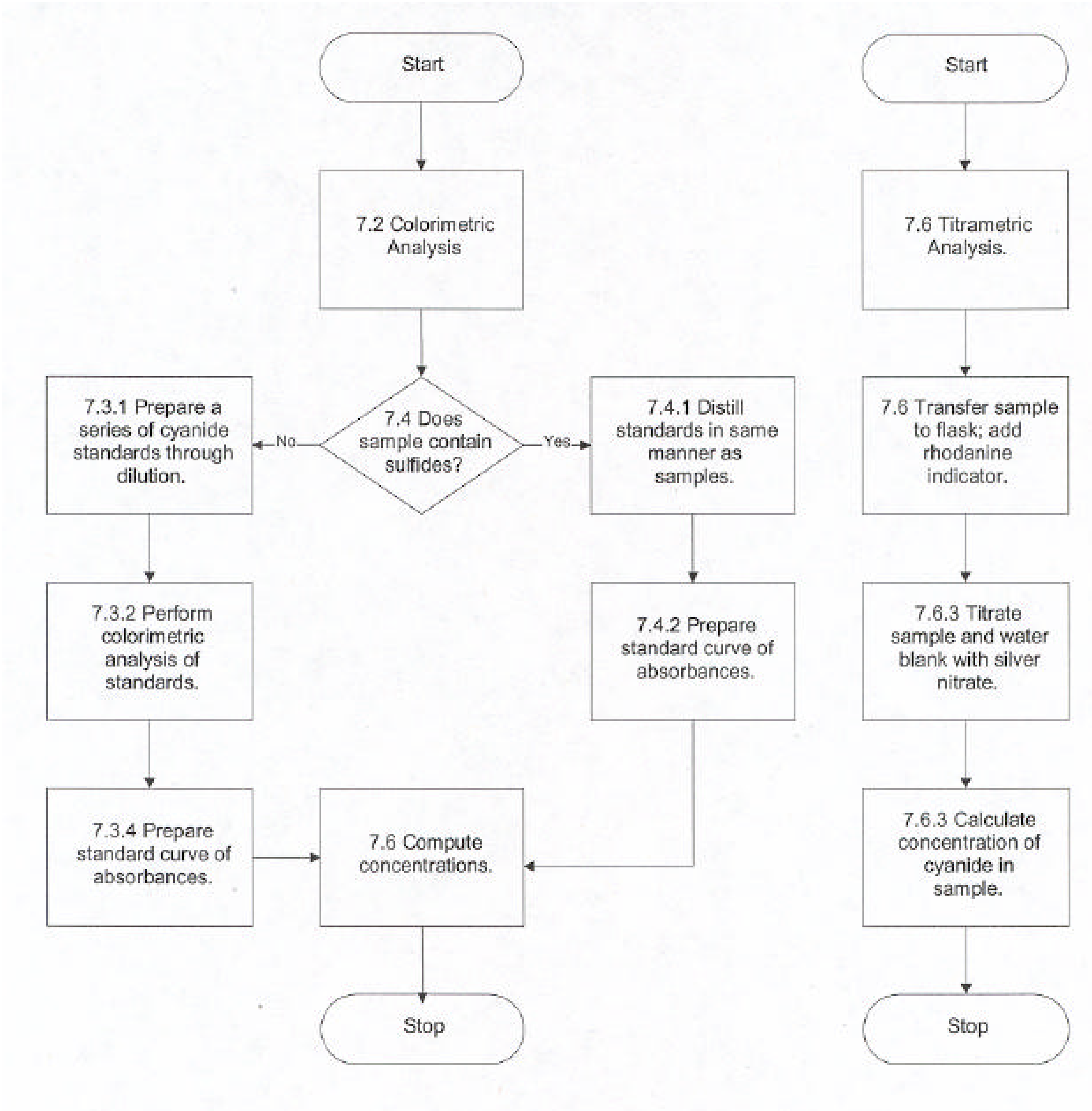
9.3 In two additional studies using surface water, ground water, and landfill leachate samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94 % and 98 .9 % for total cyanide, and 86.7 % and 97.4 % for amenable cyanide.

10.0 REFERENCES

10.1 Refer to Method 9010 for references on total and amenable cyanide.

METHOD 9014

TITRIMETRIC AND MANUAL SPECTROPHOTOMETRIC DETERMINATIVE METHODS FOR CYANIDE



3.D.4 METHOD 9034

TITRIMETRIC PROCEDURE FOR ACID-SOLUBLE AND ACID INSOLUBLE SULFIDES

1.0 SCOPE AND APPLICATION

1.1 This procedure may be used as a determinative step for acid-soluble and acid-insoluble sulfides following distillation of the sample by SW-846 Method 9030.

1.2 Method 9034 is suitable for measuring sulfide concentrations in samples which contain 0.2 mg/kg to 50 mg/kg of sulfide.

2.0 SUMMARY OF METHOD

Sulfide is extracted from the sample by a preliminary distillation procedure (See Method 9030) and precipitated in a zinc acetate scrubber as zinc sulfide. The sulfide is oxidized to sulfur by adding a known excess amount of iodine. The excess iodine is determined by titration with a standard solution of phenyl arsine oxide (PAO) or sodium thiosulfate until the blue iodine starch complex disappears. As the use of standard sulfide solutions is not possible because of oxidative degradation, quantitation is based on the PAO or sodium thiosulfate.

3 .0 INTERFERENCES

3.1 The iodometric method suffers interference from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds.

3.2 Refer to Method 9030 for a discussion of other sulfide interferences.

4.0 APPARATUS AND MATERIALS

4.1 500 mL flasks.

4.2 Hot plate stirrer.

4.3 25 mL buret.

4.4 Volumetric pipets.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as ',, defined in Chapter One.

5.3 Starch solution - Use either an aqueous solution or soluble starch powder mixtures. Prepare an aqueous solution as follows. Dissolve 2 g soluble starch and 2 g salicylic acid, C711603, as a preservative, in 100 ml, hot reagent water.

5.4 Iodine solution (approximately 0.025N)

5.5 Dissolve 25 g potassium iodide, KI, in 700 mL of reagent water in a 1-liter volumetric flask. Add 3.2 g iodine, 12. Allow to dissolve. Add the type and amount of acid specified in Section 7.3.2. Dilute to 1 liter and standardize as follows.

5.6 Dissolve approximately 2 g KI in 150 nil, of reagent water. Add exactly 20 mL of the iodine solution (Section 5.4) to be titrated and dilute to 300 ml, with reagent water.

5.6.1 Titrate with 0.025N standardized phenylarsine oxide or 0.025N sodium thiosulfate until the amber color fades to yellow. Add starch indicator solution. Continue titration drop by drop until the blue color disappears.

5.6.2 Run in replicate

5.6.3 Calculate the normality as follows.

$$\text{Normality } (I_2) = \frac{\textit{mL of titrant x normality of titrant}}{\textit{sample size in mL}}$$

5.7 Sodium sulfide nonanhydrate, Na_2S ? $9H_20$. For the preparation of standard solutions to be used for calibration curves. Standards must be prepared at pH > 9 and < 11. Protect standard from exposure to oxygen by preparing it without headspace. These standards are unstable and should be prepared daily.

5.8 Titrant.

5.8.1 Standard phenylarsine oxide solution (PAO) (0.025N), C6HSAs0. This solution is commercially available.

<u>CAUTION</u>: PAO is toxic.

5.8.2 Standard sodium thiosulfate solution (0.025N), $Na_2S_20_3$? $5H_20$. Dissolve 6.205 ± 0.005 $Na_2S_20_3$? $5H_20$ in 500 ml, reagent water. Add 9 ml, 1N NaOH and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 9030 for a discussion of sample collection, preservation, and handling.

6.2 Distillates that are not analyzed immediately should be stored in a sealed flask at ' 4°C.

7.0 PROCEDURE

7.1 The following iodometric titration procedure is used to quantify the sulfide concentration in the distillate generated by Method 9030.

7.3.1 Pipet a known amount of standardized 0.025N iodine solution (see Section 5.4) in a 500-mL flask, adding an amount in excess of that needed to oxidize the sulfide. Add enough reagent water to bring the volume to 100 mL. The volume of standardized iodine solution should be about 65 mL for samples with 50 mg of sulfide.

7.3.2 If the distillation for acid-soluble sulfide is being used, add 2 mL of 6N HCI. If the distillation for acid-insoluble sulfides is performed, 10 mL of 6N HCI should be added to the iodine.

7.3.3 Pipet the gas scrubbing solutions obtained in Method 9030 to the flask, keeping the end of the pipet below the surface of the iodine solution. If at any point in transferring the zinc acetate solution or rinsing the bottles, the amber color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Section 7.3.1 for calculations. Record the total volume of standardized 0.025N iodine solution used.

7.3.4 Prepare a rinse solution of a known amount of standardized 0.025N iodine solution, 1 ml, of 6N HCI, and reagent water to rinse the remaining white precipitate (zinc sulfide) from the gas scrubbing bottles into the flask. There should be no visible traces of precipitate after rinsing.

7.3.5 Rinse any remaining traces of iodine from the gas scrubbing bottles with reagent water, and transfer the rinsate to the flask.

7.3.6 Titrate the solution in the flask with standard 0.025N phenylarsine oxide or 0.025N sodium thiosulfate solution until the amber color fades to yellow: Add enough starch indicator for the solution to turn dark blue and titrate until the blue disappears. Record the volume of titrant used.

7.3.7 Calculate the concentration of sulfide using the following equation:

$$\underline{(\text{mL } 12 \text{ x N } 12) - (\text{mL titrant x N titrant})} \text{ x} \left[\frac{32.06g}{2\ eq.}\right] = \text{sulfide (mg/kg or mg/L}$$

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by or under supervision of experienced analysts. Refer to Method 9030 for additional quality control guidelines.

8.2 A reagent blank should be analyzed once in twenty analyses or per analytical batch, whichever is more frequent.

8.3 Check standards are prepared from water and a known amount of sodium sulfide. A check standard should be run with each analytical batch of samples, or once in twenty samples. Acceptable recovery will depend on the level and matrix.

8.4 A matrix spiked sample should be analyzed for each analytical batch or twenty samples, whichever is more frequent, to determine matrix effects. If recovery is low, acid-insoluble sulfides are indicated. A matrix spiked sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Refer to Method 9030 for data on the precision and accuracy of this method.

10.0 REFERENCES

1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 2nd ed.; U.S. Environmental Protection Agency. Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC.

2. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1979; EPA-600/4-79-020.

3. CRC Handbook of Chemistry and Physics, 66th ed.; West, R., Ed.; CRC: Boca Raton, FL, 1985.

4. Standard Methods for the Examination of Water and Wastewater, 16th ed.; Greenberg, ', A.E.; Trussell, R.R.; Clesceri, L.S., Eds.; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, DC, 1985; Methods 427, 427A, 427B, and 427D.

5. Andreae, M.O.; Banard, W.R. Anal. Chem. 1983, 55, 608-612.

6. Barclay, H. Add: Instrum. 1980, 35(2), 59-61.

7. Bateson, S.W.; Moody, G.J.; Thomas, J.P.R. Analyst 1986, 111, 3-9.

8. Berthage, P.O. Anal. Chim. Acta 1954, 10 310-311.

9. Craig, P.J.; Moreton, P.A. Environ. Technol. Lett. 1982, 3, 511-520.

10. Franklin, G.O.; Fitchett, A.W. Pulp & Paper Canada 1982, 83(10), 40-44.

11. Fuller, W. In Cyanide in the Environment; Van Zyl, D., Ed.; Proceedings of Symposium; December, 1984.

12. Gottfried, G.J. "Precision, Accuracy, and MDL Statements for EPA Methods 9010, 9030, 9060, 7520, 7521, 7550, 7551, 7910, and 7911"; final report to the U.S. Environmental Protection Agency (EMSL-CI); Biopheric.

13. Kilroy, W.P. Talanta 1983, 30(6), 419-422.

14. Kurtenacher, V.A.; Wallak, R. Z. Anor . U. Ally. Chem. 1927, 161 202-209.

15. Landers, D.H.; David, M.B.; Mitchell, M.J. Int. J. Anal. Chem 1983, 14, 245-256.

16. Opekar, F.; Brukenstein, S. Anal. Chem. 1984, 56, 1206-1209.

17. Ricklin, R.D.; Johnson, E.L. Anal. Chem. 1983, 55, 4.

18. Rohrbough, W. G. ; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

19. Snedecor, G.W.; Ghran, W.G. Statistical Methods; Iowa State University: Ames, IA, 1980.

20. Umana, M.; Beach, J.; Sheldon, L. "Revisions to Method 9010"; final report to the U.S. Environmental Protection Agency on Contract No. 68-01-7266; Research Triangle Institute: Research Triangle Park, NC, 1986; Work Assignment No. 1.

21. Umana, M.; Sheldon, L. "Interim Report: Literature Review"; interim report to the U.S. Environmental Protection Agency in Contract No. 68-01-7266; Research Triangle Institute: Research Triangle Park, NC, 1986; Work Assignment No. 3.

22. Wang, W.; Barcelona, M.J. Environ. Inter. 1983, 9, 129-133.

23. Wronski, M. Talanta 1981, 28, 173-176.

24. Application Note 156; Princeton Applied Research Corp.: Princeton, NJ.

25. Guidelines for Assessing and Reporting Data Quality for Environmental Measurements; U.S. Environmental Protection Agency. Office of Research and Development. U.S. Government Printing Office: Washington, DC, 1983.

26. Fed. Regist. 1980, 45(98), 33122.

27. The Analytical Chemistry of Sulfur and Its Compounds, Part I; Karchmer, J.H., Ed.; Wiley-Interscience: New York, 1970.

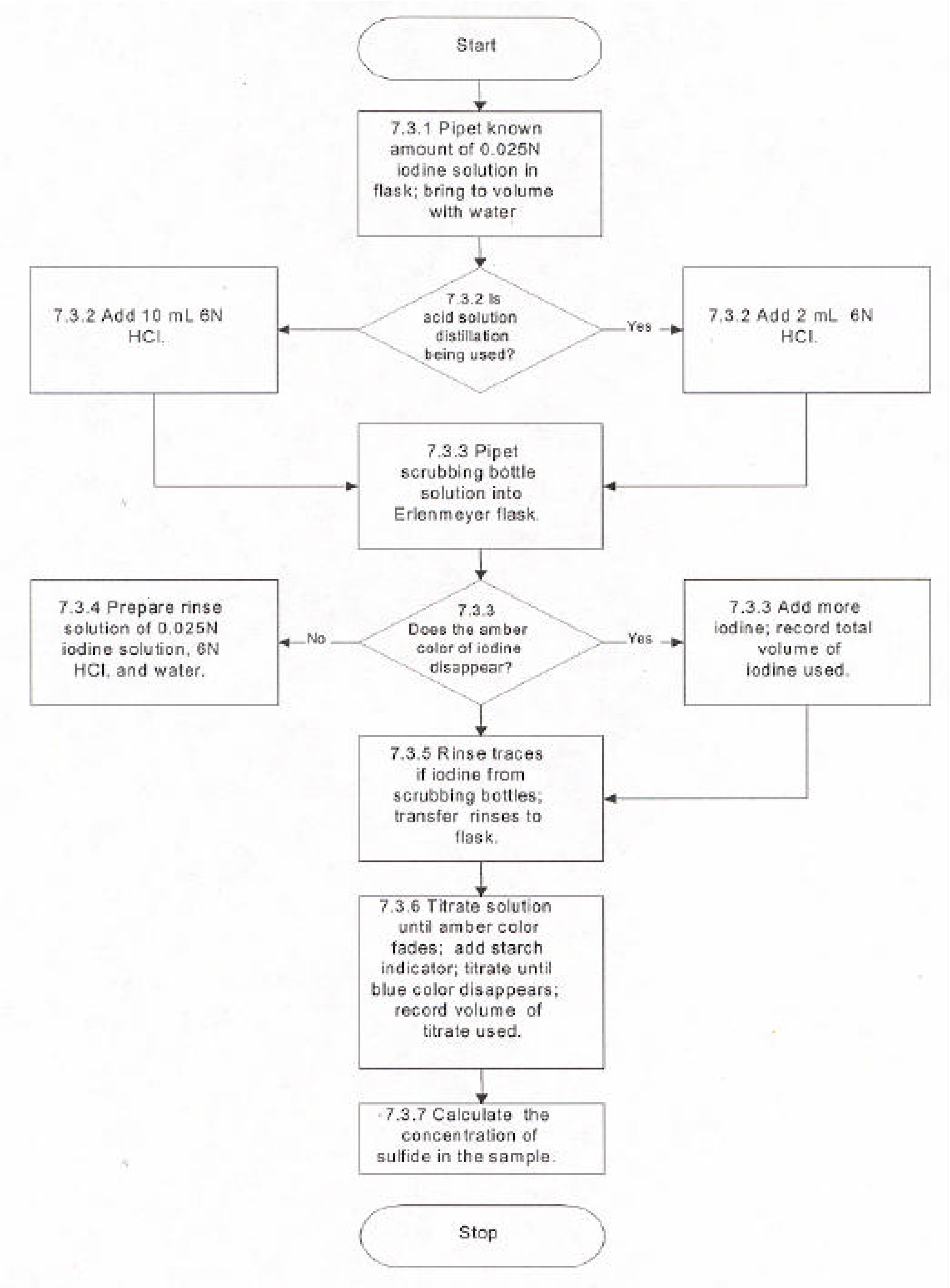
28. Methods for the Examination of Water and Associated Materials; Department of the Environment: England, 1983.

29. "Development and Evaluation of a Test Procedure for Reactivity Criteria for Hazardous Waste"; final report to the U.S. Environmental Protection Agency on Contract 68 03-2961; EAL: Richmond, CA.

30. Test Method to Determine Hydrogen Sulfide Released from Wastes; U.S. Environmental Protection Agency. Office of Solid Waste. Preliminary unpublished protocol, 1985.

31. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 9034
TITRIMETRIC PROCEDURE FOR ACID-SOLUBLE
AND ACID INSOLUBLE SULFIDES



3. E.1 METHOD 1311

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

1.3 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.0 SUMMARY OF METHOD

2.1 For liquid wastes (i.e., those containing less than 0.5 percent dry solid material), the waste, after filtration through a 0.6 to 0.8 pm glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than or equal to 0.5 percent solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 pm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels

4.2.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of volatile analytes i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Section 4.3.1). The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[4] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to I, be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Section 7.3) refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is .measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

[4] VITON® is a trademark of Du Pont.

4.2.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Section 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Section 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in Section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

> NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Section 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (less thanl0percent) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4:

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern..

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 gm, or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with IN nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to ± 0.05 units at 25 degrees C.

4.6 ZHE Extract Collection Devices: TEDLAR®5 bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., less than 1 percent of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., greater than 1 percent of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100 percent solid) or has no significant phase (is 100 percent liquid), either the TEDLAR© bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.~., a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (see Section 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

---

5 TEDLAR® is a registered trademark of Du Pont.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.2.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.2.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 ± S degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.3 Hydrochloric acid (1N), HC I, made from ACS reagent grade.

5.4 Nitric acid (1N), $HN0_3$ made from ACS reagent grade.

5.5 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.6 Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade.

5.7 Extraction fluid.

5.7.1 Extraction fluid # 1: Add 5.7 mL glacial CH3CHZOOH to 500 mL of reagent water (See Section 5.2), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05. , 5.7.2 Extraction fluid # 2: Dilute 5.7 mL glacial CH3CHZOOH with reagent water (See Section 5.2) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 ± 0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.8 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction (see Section 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4 degrees C. Samples should be opened only immediately prior to extraction).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH less than 2, unless precipitation occurs (see Section 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 8.0 (QA requirements) for acceptable sample and extract holding times.

7.0 PROCEDURE

7.1 Preliminary Evaluations

Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids (Section 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Section 7.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (Section 7.1.4).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (Le., is 100 percent solids) proceed to Section 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered I followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 degrees C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

> NOTE: If waste material (greater than 1 percent of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.1.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

> NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

> NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Section 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Section 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Section 7.1.1.9)}}{\text{Total weight of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Section 7.1.1.9 is equal to or greater than 0.5 percent, then proceed either to Section 7.1.3 to determine whether the solid material requires particle size reduction or to Section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Section 7.1.1.9 is less than 0.5 percent, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed and to Section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 ± 20 degrees C until two successive weighing yield the same value within ± 1 percent. Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Wt. of dry waste + filter) - tared wt. of filter}}{\text{Initial wt. of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5 percent, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed, and to Section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5 percent, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 7.1.3) and determine the appropriate extraction fluid (Section 7.1.4). If only the volatile TCLP is to be performed, see the note in Section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm2 , or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions musts be taken (see Section 7.3.6).

> NOTE: Surface area criteria are meant for filamentous (e.~., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5 percent and if the sample will be extracted for nonvolatile constituents (Section 7.2), determine the appropriate fluid (Section 5.7) for the nonvolatiles extraction as follows:

> NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1 (Section 5.7.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to Section 7.3.

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is less than 5.0, use extraction fluid #1. Proceed to Section 7.2.

7.1.4.3 If the pH from Section 7.1.4.2 is greater than 5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50 degrees C, and hold at 50 degrees C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is less than 5.0, use extraction fluid #1. If the pH is greater than 5.0, use extraction fluid #2. Proceed to Section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation (Sections 7.1.1 - 7.1.4) was determined to be 100 percent solid at Section 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Section 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Section 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Section 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Section 7.2.10 of the nonvolatile TCLP extraction.

Procedure When Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration e.g., is 100 percent solid, see Section 7.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to Section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains less than 0.5 percent dry solids (Section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing greater than 0.5 percent dry solids (Sections 7.1.1 or 7.1.2), use the percent solids information obtained in Section

7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Section 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 degrees C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample

> NOTE: If waste material (greater than 1 percent of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.2.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (Le., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

> NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See Section 7.2.12) or stored at 4 degrees C until time of analysis.

> NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the waste contains less than 0.5 percent dry solids (see Section 7.1.2), proceed to Section 7.2.13. If the waste contains greater than 0.5 percent dry solids (see Section 7.1.1 or 7.1.2), and if particle size reduction of the solid was needed in Section 7.1.3, proceed to Section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 7.2.11.

7.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

> NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Section 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2 degrees C during the extraction period.

> NOTE; As agitation continues; pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filters) shall be acid-washed (see Section 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the TCLP extract as follows:

7.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.2.12 is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.2 If compatible e. ., multiple phases will not result on combination), combine the filtered liquid resulting from Section 7.2.12 with the initial liquid phase of the waste obtained in Section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Section 7.2.7, is not or may not be compatible with the filtered liquid resulting from Section 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCCLP extract, and combine the results mathematically, as described in Section 7.2.14.

7.2.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots musts be acidified with nitric acid to pH less than 2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots musts be stored under refrigeration (4 degrees C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ± 0.5 percent), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).

C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second place (mg/L).

7.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles are Involved

Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes ~., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.'

Do not allow the waste, the initial phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4 degrees C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (See Section 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis.. The containers listed in Section 4.6 are recommended for use under the conditions stated in Sections 4.6.1 - 4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 7.3, Section 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the waste is 100 percent solid (see Section 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Section 7.3.5.

7.3.4 If the waste contains less than 0.5 percent dry solids (Section 7.1.2), the liquid portion of waste, after filtration, is defined as the TCLCP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing greater than or equal to 0.5 percent dry solids (Sections 7.1.1 and/or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum samp le size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For wastes containing less than 5 percent solids (see Section 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing greater than or equal to 5 percent solids (see Section 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Section 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle size reduction of the solid portion of the waste was required in Section 7.1.3, proceed to Section 7.3.6. If particle size reduction was not required in Section 7.1.3, proceed to Section 7.3.7.

7.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid' portion of the waste to a surface area or particle size as described in Section 7.1.3. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4 degrees C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to Section 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

> NOTE: If waste material (greater than 1 percent of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Section 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 degrees C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100 percent solid (see Section 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Section 7.3.12.

7.3.9 Attach the evacuated pre-weighted filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 5O psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

> NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

> NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained less than 0.5 percent dry solids (see Section 7.1.2), this filtrate is defined as the TCCLP extract and is analyzed directly. Proceed to Section 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (See Sections 7.3.13 through 7.3.15) or stored at 4 degrees C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \text{ x percent solids}_{\text{(Section 7.1.1)}} \text{ x weight of waste filtered}_{\text{(Section 7.3.4 or 73.8)}}}{100}$$

7.3.12 The following Sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Section 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the, extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary agitation apparatus (if it is not already there) and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 ± 2 degrees C during agitation.

7.3.13 Following the 18 ± 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i-e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Section 4.2.1, and perform II, the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container i.e., TEDLAR® I bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Section 7.3.9. All extract shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Sections 4.6 and 7.3.1).

> NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.3.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.3.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Section 7.3.13 and the initial liquid phase (Section 7.3.9) are collectively defined as the TCLP extract.

7.3.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4 degrees C until analyzed. Analyze the III TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5 percent), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1+V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

8.0 QUALITY ASSURANCE

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel.

8.2 A matrix spike shall be performed for each waste type (e~., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to demonstrate teat the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

8.2.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

percentR (percentRecovery) -100 (X_S – X_u)/K

where:
X_S = measured value for the spiked sample,
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50 percent and the concentration does not exceed the regulatory level, and (2) the concentration of the contaminant measured in the extract is within 20 percent of the appropriate regulatory level.

8.4.1 The method of standard additions shall be employed as the internal' calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The fourth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50 percent of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100 percent and 150 percent of the expected concentration of the sample. All four aliquots are maintained at the same final volume by ' adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependent variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentrations as the dependent variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo TCLP extraction within the following time periods:'

SAMPLE MAXIMUM HOLDING TIMES [Days] _				
	From: Field Collection To: TCLP extraction	From: TCLP Extraction To: Preparative extraction	From: Preparative Extraction To: Determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not-:applicable

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.0 METHOD PERFORMANCE

9.1 Ruggedness. Two ruggedness studies have been performed to determine the effect of various perturbations on specific elements of the TCLP protocol. Ruggedness testing determines the sensitivity of small procedural variations which might be expected to occur during routine laboratory application.

9.1.1 Metals - The following conditions were used when leaching a waste for metals analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Extraction time	16 hours vs. 18 hours
Headspace	20 percent vs. 60 percent
Buffer #2 acidity	190 meq vs. 210 meq
Acid-washed filters	yes vs. no
Filter type	0.7 µm glass fiber vs. 0.45 µm vs. polycarbonate
Bottle type	borosilicate vs. flint glass

Of the seven method variations examined, acidity of the extraction fluid had the greatest impact on the results. Four of 13 metals from an API separator sludge/electroplating waste (API/EW) mixture and two of three metals from an ammonia lime still bottom waste were extracted at higher levels by the more acidic buffer. Because of the sensitivity to pH changes, the method requires that the extraction fluids be prepared so that the final pH is within ± 0.5 units as specified.

9.1.2 Volatile Organic Compounds - The following conditions were used when leaching a waste for VOC analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Headspace	0 percent vs. 5 percent
Buffer #1 acidity	60 meq vs. 80 meq
Method of storing extract	Syringe vs. Tedlar® bag
Aliquotting	yes vs. no
Pressure behind piston	0 psi vs. 20 psi

None of the parameters had a significant effect on the results of the ruggedness test.

9.2 Precision. Many TCLP precision (reproducibility) studies have been performed, and have shown that, in general, the precision of the TCLP is comparable to or exceeds that of the EP toxicity test and that method precision is adequate. One of the more significant contributions to poor precision appears to be related to sample homogeneity and inter--°laboratory variation (due to the nature of waste materials).

9.2.1 Metals - The results of a multi-laboratory study are shown in Table 6, and indicate that a single analysis of a waste may not be adequate for waste characterization and identification requirements.

9.2.2 Semi-Volatile Organic Compounds - The results of two studies are shown in Tables 7 and 8. Single laboratory precision was excellent with greater than 90 percent of the results exhibiting an RSD less than 25 percent. Over 85 percent of all individual compounds in the multi-laboratory study ell in the RSD range of 20 - 120 percent. Both studies concluded that the TCLP provides adequate precision. It was also determined that the high acetate content of the extraction fluid did not present problems (i.e., column degradation of the gas chromatography for the analytical conditions used.

9.2.3 Volatile Organic Compounds - Eleven laboratories participated in a collaborative study of the use of the ZHE with two waste types which were fortified with a mixture of VOCs. The results of the collaborative study are shown in Table 9. Precision results for VOCs tend to occur over a considerable range. However, the range and mean RSD compared very closely to the same collaborative study metals results in Table 6. Blackburn and Show concluded that at the 95 percent level of significance: 1) recoveries among laboratories were statistically similar, 2) recoveries did not vary significantly between the two sample types, and 3) each laboratory showed the same pattern of recovery for each of the two samples.

10.0 REFERENCES

1. Blackburn, W.B. and Show, I. "Collaborative Study of the Toxicity Characteristics Leaching Procedure (TCLP)." Draft Final Report, Contract No. 68-03-1958, S-Cuted, November 1986.

2. Newcomer, L.R., Blackburn, W.B., Kimmell, T.A. "Performance of the Toxicity Characteristic Leaching Procedure." Wilson Laboratories, S-Cubed, U.S. EPA, December 1986.

3. Williams, L.R., Francis, C.W.; Maskarinec, M.P., Taylor D.R., and Rothman, N. "Single-Laboratory Evaluation of Mobility Procedure for Solid Waste." EMSL, ORNL, S Cubed, ENSECO.

Table 1
Volatile Analytes[1,2]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2,-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	133-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

[2] Benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene, and vinyl chloride are toxicity characteristic constituents.

Table 2.
Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S) 8-vessel extractor (DC20) 12-vessel extractor (DC20B) 24-vessel extractor (DC240C)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2-BRE) 4-vessel (3740-4-BRE) 6-vessel (3740-6-BRE) 8-vessel (3740-8-BRE) 12-vessel (3740-12-BRE) 24-vessel (3740-24-BRE)
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitemore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (SVRE) 6-vessel (6VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 2-liter bottle extractor (YT31 ORAHW)

[1]Any device that rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

Table 3.

Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C 102, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing2	Whitemore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30090HW, Gas Pressure Device
Environmental Machine and Design; Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOXI, Gas Pressure Device
Gelman Science	Ann Arbor, MI (800) 521-1520	15400 Gas Pressure Device

[1]Any device that meets the specifications listed in Section 4.2.1 of the method is suitable.

[2]This device uses a 110 mm filter.

Table 4.
Suitable Filter Holders[1]

Company	Model/ Location	Catalogue No.	Size
Nucleopore Corporation	Pleasanton, CA	425910	124 mm
	(800) 882-7711	410400	47 mm
Micro Filtration Systems	Dublin, CA	302400	142 mm
	(800) 334-7132	311400	-47 mm
	(41 S) 828-6010		
Millipore Corporation	Bedford, MA	XT30142HW	124 mm
	(800) 225-3384	XX1004700	47 mm

[1]Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5.
Suitable Filter Media[1]

Company	Location	Model	Pore Size (µm)
Millipore Corporation (800) 225-3384	Bedford, MA	AP40	0.7
Nucleopore Corporation (415) 463-2530	Pleasanton, CA	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7
Gelman Science	Ann Arbor, MI (800) 521-1520	66256 (90mm) 66257 (142mm)	0.7

[1]Any filter that meets the specifications in Section 4.4 of the Method is suitable.

Table 6. Mufti-Laboratory TCLP Metals, Precision

Waste	Extraction Fluid	Metal	X	S	percentRSD
Ammonia	#1	Cadmium	0.053	0.031	60
Lime Still	#2		0.023	0.017	76
Bottoms	#1	Chromium	0.015	0.0014	93
	#2		0.0032	0.0037	118
	#1	Lead	0.0030	0.0027	90
	#2		0.0032	0.0028	87
API/EW-	#1	Cadmium	0.0046	0.0028	61
Mixture	#2		0.0005	0.0004	77
	#1	Chromium	0.0561	0.0227	40
	#2		0.105	0.018	17
	#1	Lead	0.0031	0.0031	100
	#2		0.0124	0.0136	110
Fossil	#1	Cadmium	0.080	0.069	86
Fuel Fly	#2		0.093	0.067	72
Ash	#1	Chromium	0.017	0.014	85
	#2		0.070	0.040	57
	#1	Lead	0.0087	0.0074	85
	#2		0.0457	0.0083	18
					percentRSD Range =17 - 118 Mean percentRSD = 74

NOTE: X = Mean results from 6 - 12 different laboratories
Units = mg/L
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 7. Single-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	X	S	Percent RSD
Ammonia	Phenol	#1	19000	2230	11.6
Lime Still		#2	19400	929	4.8
Bottoms	2-Methylphenol	#1	2000	297	14.9
		#2	1860	52.9	2.8
	4-Methylphenol	#1	7940	1380	17.4
		#2	7490	200	2.7
	2,4-Dimethylphenol	# 1	321	46.8	14.6
		#2	307	45.8	14.9
	Naphthalene	#1	3920	413	10.5
		#2	3827	176	4.6
	2-Methylnaphthalene	#1	290	44.8	15.5
		#2	273	19.3	7.1
	Dibenzofuran	#1	187	22.7	12.1
		#2	187	7.2	3.9
	Acenaphthylene	#1	703	89.2	12.7
		#2	663	20.1	3.0
	Fluorene	#1	151	17.6	11.7
		#2	156	2.1	1.3
	Phenanthrene	#1	241	22.7	9.4
		#2	243	7.9	3.3
	Anthracene	#1	33.2	6.19	18.6
		#2	34.6	1.55	4.5
	Fluoranthrene	#1	25.3	1.8	7.1
		#2	26.0	1.8	7.1
API/EW	Phenol	#1	40.7	13.5	33.0
Mixture		#2	19.0	1.76	9.3
	2,4-Dimethylphenol	#1	33.0	9.35	28.3
		#2	43.3	8.61	19.9
	Naphthalene	#1	185	29.4	15.8
		#2	165	24.8	15.0
	2-Methylnaphthalene	#1	265	61.2	23.1
		#2	200	18.9	9.5
					percentRSDRange = 1 - 33 Mean percentRSD - 12

NOTE: Units = µg/L

Extractions were performed in triplicate

All results were at least 2x the detection limit

Extraction Fluid # 1 = pH 4.9

#2 = pH 2.9

Table 8. Mufti-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	X	S	Percent RSD
Ammonia Lime	BNAs	#1	10043	7680	76.5
Still Bottoms (A)		#2	10376	6552	63.1
API/EW	BNAs	#1	1624	675	41.6
Mixture (B)		#2	2074	1463	70.5
Fossil Fuel	BNAs	#1	750	175	23.4
Fly Ash (C)		#2	739	342	46.3
					Mean percentRSD = 54

NOTE: Units = µg/L
X = Mean results from 3 - 10 labs
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

percentRSD Range for Individual Compounds

A, #1	0 - 113
A, #2	28 - 108
B, #1	20 - 156
B, #2	49 - 128
C, #1	36 - 143
C, #2	61 - 164

Table 9. Mufti-Laboratory (11 Labs) VOCs, Precision

Waste	Compound	X	S	percentRSD
Mine Tailings	Vinyl chloride	6.36	6.36	100
	Methylene chloride	12.1	11.8	98
	Carbon disulfide	5.57	2.83	51
	l,l-Dichloroethene	21.9	27.7	127
	1,1-Dichloroethane	31.4	25.4	81
	Chloroform	46.6	29.2	63
	1,2,-Dichloroethane	47.8	33.6	70
	2-Butanone	43.5	36.9	85
	1,1,1-Trichloroethane	20.9	20.9	100
	Carbon tetrachloride	12.0	8.2	68
	Trichloroethene	24.7	21.2	86
	1,1,2-Trichloroethene	19.6	10.9	56
	Benzene	37.9	28.7	76
	1,1,2,2-Tetrachloroethane	34.9	25.6	73
	Toluene	29.3	11.2	38
	Chlorobenzene	35.6	19.3	54
	Ethylbenzene	4.27	2.80	66
	Trichlorofluoromethane	3.82	4 40	115
	Acrylonitrile	76.7	110.8	144
Ammonia Lime Still Bottoms	Vinyl chloride	5.00	4.71	94
	Methylene chloride	14.3	13.1	92
	Carbon disulfide	3.37	2.07	61
	1,1,-Dichoroethene	52.1	38.8	75
	l,l-Dichloroethane	52.8	25.6	49
	Chloroform	64.7	28.4	44
	1,2-Dichloroetehane	43.1	31.5	73
	2-Butanone	59.0	39.6	67
	1,1,1-Trichloroethane	53.6	40.9	76
	Carbonn tetrachlordie	7.10	6.1	86
	Trichloroethene	57.3	34.2	60
	1,1,2-Trichloroethene	6.7	4.7	70
	Benzene	61.3	26.8	44
	1;1,2,2-Tetrachloroethane	3.16	2.1	66
	Toluene	69.0	18.5	27
	Chlorobenzene	71.8	12.0	17
	Ethylbenzene	3.70	2.2	58
	Trichlorofluoromethane	4.05	4.8	119
	Acrylonitrile	29.4	34.8	118
				percentRSD Range = 17 - 144
				Mean percentRSD = 75

NOTE: Units= µg/L

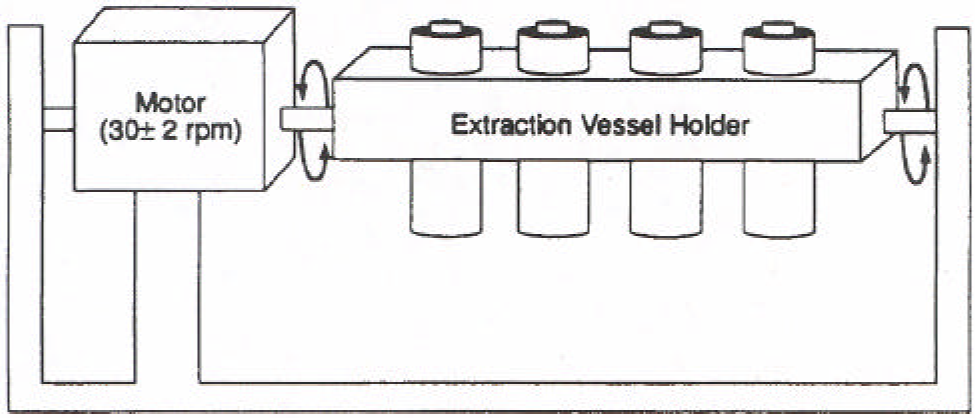


Figure 1. Rotary Agitation Apparatus

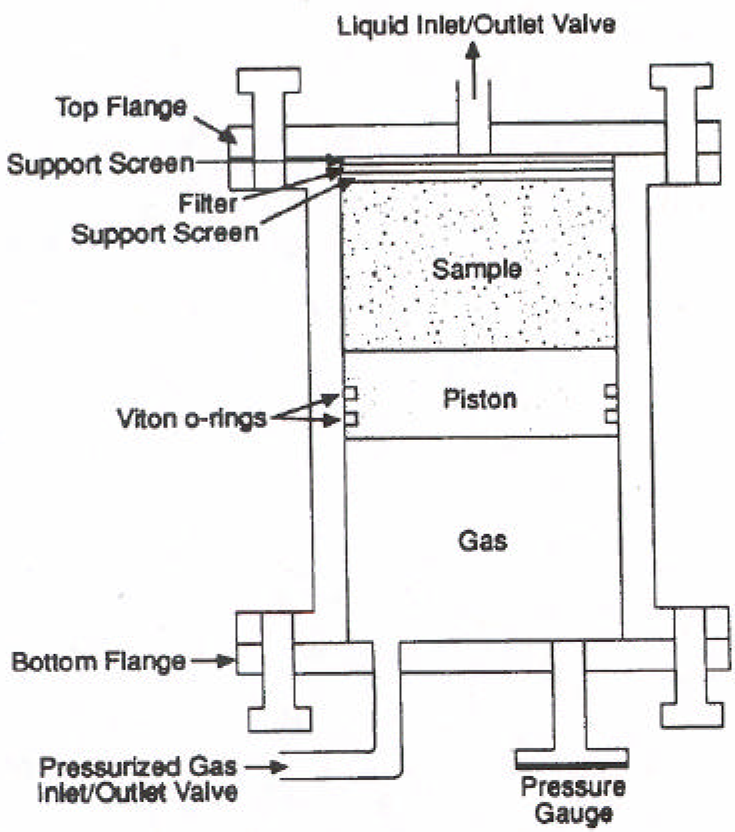
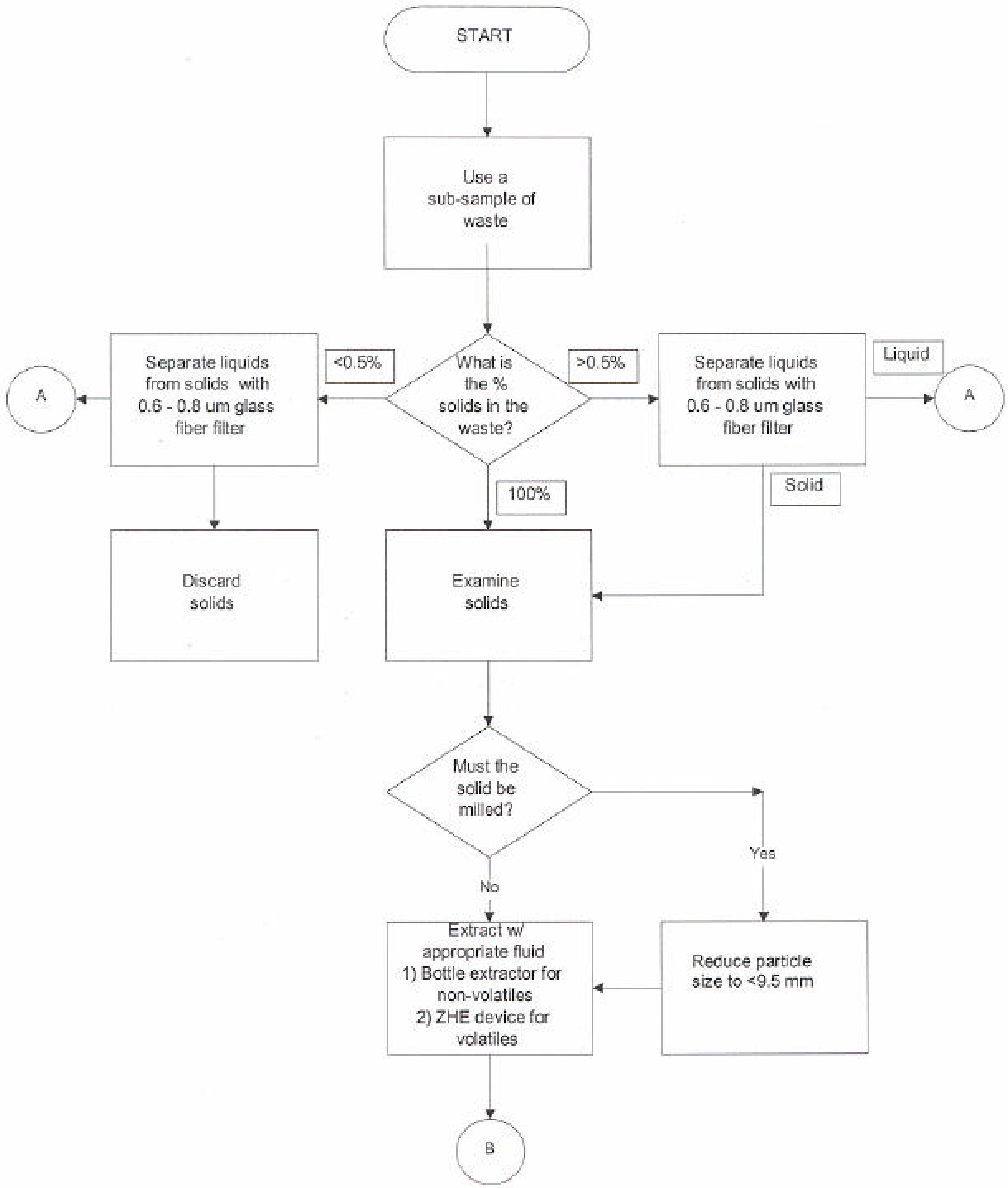
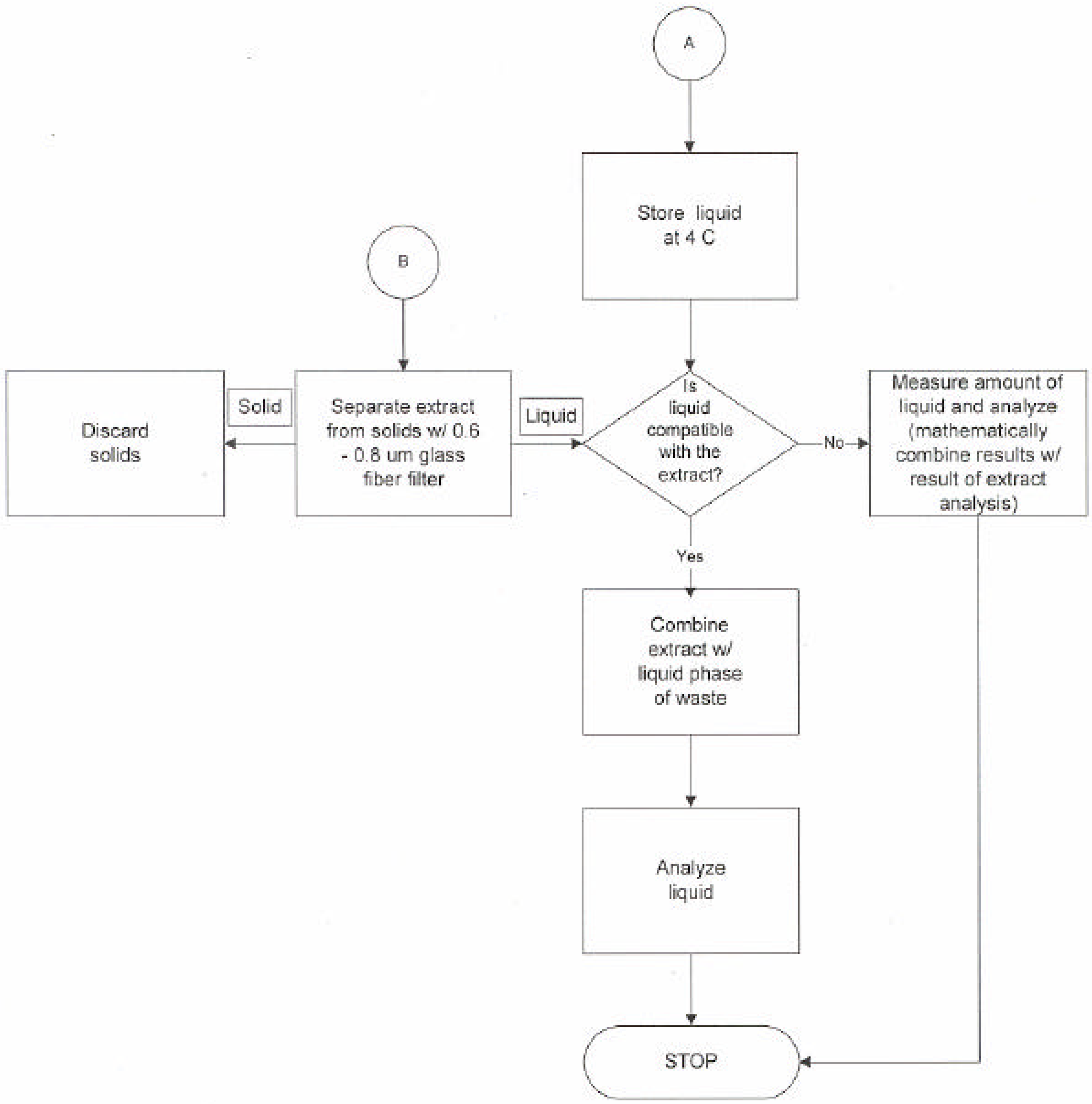


Figure 2. Zero-Headspace Extractor (ZHE)

Method 1311
Toxicity Characteristic Leachate Procedure



Method 1311
Toxicity Characteristic Leachate Procedure continued



3.F.1 METHOD 9076

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY PRODUCTS BY OXIDATIVE COMBUSTION AND MICROCOULOMETRY

1.0 SCOPE AND APPLICATION

1.1 This test method covers the determination of total chlorine in new and used oils, fuels and related materials, including crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by oxidative combustion and microcoulometry. The chlorine content of petroleum products is often required prior to their use as a fuel.

1.2 The applicable range of this method is from 10 to 10,000 µg/g chlorine.

2.0 SUMMARY OF METHOD

2.1 The sample is placed in a quartz boat at the inlet of a high-temperature quartz combustion tube.-An inert carrier gas such as argon, carbon dioxide, or nitrogen sweeps across the inlet while oxygen flows into the center of the combustion tube. The boat and sample are advanced into a vaporization zone of approximately 300 degrees C to volatilize the light ends. Then the boat is advanced to the center of the combustion tube, which is at 1,000 degrees C. The oxygen is diverted to pass directly over the sample to oxidize any remaining refractory material. All during this complete combustion cycle, the chlorine is converted to chloride and oxychlorides, which then flow into an attached titration cell where they quantitatively react with silver ions. The silver ions thus consumed are coulometrically replaced. The total current required to replace the silver ions is a measure of the chlorine present in the injected samples.

2.2 The reaction occurring in the titration cell as chloride enters is:

$$CI^- + Ag^+ \dashrightarrow AgCI \qquad (1)$$

The silver ion consumed in the above reaction is generated coulometrically thus:

$$Ag^0 \dashrightarrow Ag^+ + e- \qquad (2)$$

2.3 These microequivalents of silver are equal to the number of micro-equivalents of titratable sample ion entering the titration cell.

3.0 INTERFERENCES

3.1 Other titratable halides will also give a positive response. These titratable halides include **HBr and HI (HOBr + HOI** do not precipitate silver). Because these oxyhalides do not react in the titration cell, approximately 50% microequivalent response is detected from bromine and iodine.

3.2 Fluorine as fluoride does not precipitate silver, so it is not an interferant nor is it detected.

3.3 This test method is applicable in the presence of total sulfur concentrations of up to 10,000 times the chlorine level.

4.0 APPARATUS AND MATERIALS[6]

4.1 Combustion furnace. The sample should be oxidized in an electric furnace capable of maintaining a temperature of 1,000 degrees C to oxidize the organic matrix.

4.2 Combustion tube, fabricated from quartz and constructed so that a sample, which is vaporized completely in the inlet section, is swept into the oxidation zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube connects to a boat insertion device where the sample can be placed on a quartz boat by syringe, micropipet, or by being weighed externally. Two gas ports are provided, one for an inert gas to flow across the boat and one for oxygen to enter the combustion tube.

4.3 Microcoulometer, Stroehlein Coulomat 702 CL or equivalent, having variable gain and bias control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. The microcoulometer output signal shall be proportional to the generating current. The microcoulometer may have a digital meter and circuitry to convert this output signal directly to a mass of chlorine (e.g., nanograms) or to a concentration of chlorine (e.g., micrograms of chlorine or micrograms per gram).

4.4 Titration cell. Two different configurations have been applied to coulometrically III
titrate chlorine for this method.

4.4.1 Type I uses a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain constant silver ion concentration and an inlet for a gaseous sample from the pyrolysis tube. The sensor, reference, and anode electrodes are silver electrodes. The cathode electrode is a platinum wire. The reference electrode resides in a saturated silver acetate half-cell. The electrolyte contains 70 percent acetic acid in water.

4.4.2 Type II uses a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain

6 Any apparatus that meets the performance criteria of this section may be used to conduct analyses by this methodology. Three commercial analyzers that fulfill the requirements for apparatus Steps 4.1 through 4.4 are: Dohrmann Models DX-20B and MCTS-20 and Mitsubishi Model TSX-10 available from Cosa Instrument.

constant silver ion concentration, an inlet for a gaseous sample that passes through a 95 percent sulfuric acid dehydrating tube from the pyrolysis tube, and a sealed two-piece titration cell with an exhaust tube to vent fumes to an external exhaust. All electrodes can be removed and replaced independently without reconstructing the cell assembly. The anode electrode is constructed of silver. The cathode electrode is constructed of platinum. The anode is separated from the cathode by a 10 percent KN03 agar bridge, and continuity is maintained through an aqueous 10 percent KN03 salt bridge. The sensor electrode is constructed of silver. The reference electrode is a silver/silver chloride ground glass sleeve, double junction electrode with aqueous 1M KN03 in. the outer chamber and aqueous 1M KCl in the inner chamber.

4.5 Sampling syringe, a microliter syringe of 10 AL capacity capable of accurately delivering 2 to 5 /µL of a viscous sample into the sample boat.

4.6 Micropipet, a positive displacement micropipet capable of accurately delivering 2 to 5 µL of a viscous sample into the sample boat.

4.7 Analytical balance. When used to weigh a sample of 2 to 5 mg onto the boat, the balance shall be accurate to + 0.01 mg. When used to determine the density of the sample, typically 8 g per 10 mL, the balance shall be accurate to + 0.1 g.

4.8 Class A volumetric flasks: 100 mL.

5.0 REAGENTS

5.1 Purity of Reagents. Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Acetic acid, $CH_3\ CO_2H$. Glacial.

5.4 Isooctane, $(CH_3)_2\ CHCH_2\ C(CH_3)_3$ (2,2,4-Trimethylpentane).

5.5 Chlorobenzene, C_6H_5 C1.

5.6 Chlorine, standard stock solution - 10,000 ng Cl/µL, weigh accurately 3.174 g of chlorobenzene into 100-mL Class A volumetric flask. Dilute to the mark with isooctane.

5.7 Chlorine, standard solution. 1,000 ng Cl/µL, pipet 10.0 mL of chlorine stock solution (Sec. 5.6) into a 100-mL volumetric flask and dilute to volume with isooctane.

5.8 Argon, helium, nitrogen, or carbon dioxide, high-purity grade (HP) used as the carrier gas. High-purity grade gas has a minimum purity of 99.995 percent.

5.9 Oxygen, high-purity grade (HP), used as the reactant gas.

5.10 Gas regulators. Two-stage regulator must be used on the reactant and carrier gas.

5.11 Cell Type 1.

5.11.1 Cell electrolyte solution. 70 percent acetic acid: combine 300 mL reagent water with 700 mL acetic acid (Sec. 5.3) and mix well.

5.11.2 Silver acetate, CH3 COZ Ag. Powder purified for saturated reference electrode.

5.12 Cell Type 2.

5.12.1 Sodium acetate, CH_3 $C0_2$ Na.

5.12.2 Potassium nitrate, $KN0_3$.

5.12.3 Potassium chloride, KCI.

5.12.4 Sulfuric acid (concentrated), H_2 $S0_4$.

5.12.5 Agar, (jelly strength 450 to 600 g/cm^2).

5.12.6 Cell electrolyte solution - 85 percent acetic acid: combine 150 mL reagent water with 1.35 g sodium acetate (Sec. 5.12.1) and mix well; add 850 mL acetic acid (Sec. 5.3) and mix well.

5.12.7 Dehydrating solution - Combine 95 mL sulfuric acid (Sec. 5.12.4) with 5 mL reagent water and mix well.

CAUTION: This is an exothermic reaction and may proceed with bumping unless controlled by the addition of sulfuric acid. Slowly add sulfuric acid to reagent water. Do not add water to sulfuric acid.

5.12.8 Potassium nitrate (10 percent), KN03 . Add 10 g potassium nitrate (Sec. 5.12.2) to 100 mL reagent water and mix well.

5.12.9 Potassium nitrate (1M), KN03 . Add 10.11 g potassium nitrate (Sec. 5.12.2) to 100 mL reagent water and mix well.

5.12.10 Potassium chloride (1M), KCI. Add 7.46 g potassium chloride (Sec.

5.12.3) to 100 ml, reagent water and mix well.

5.12.11 Agar bridge solution - Mix 0.7 g agar (Sec. 5.12.5), 2.5g potassium nitrate (Sec. 5.12.2), and 25 mL reagent water and heat to boiling.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Because the collected sample will be analyzed for total halogens, it should be kept headspace free and refrigerated prior to preparation and to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

6.3 Laboratory subsampling of the sample should be performed on a well-mixed sample of oil.

7.0 PROCEDURES

7.1 Preparation of apparatus.

7.1.1 Setup the analyzer as per the equipment manufacturer's instructions.

7.1.2 Typical operating conditions: Type 1.

Furnace temperature ....1,000 degrees C
Carrier gas flow ....43 cm^3/min
Oxygen gas flow ....160 cm^3/min
Coulometer Bias ....250 mV
Gain..25 percent

7.1.3 Typical operating conditions: Type 2.

Furnace temperature	H-1 850 degrees C
Furnace temperature	H-2 1,000 degrees C
Carrier gas flow	250 cm^3/min
Oxygen gas flow	250 cm^3/min
Coulometer End point potential (bias)	300 mV
Gain G-1	1.5 coulombs/ change in mV
Gain G-2	3.0 coulombs/ change in mV
Gain G-3	3.0 coulombs/ change in mV
ES-1 (range 1)	25 mV
ES-2 (range 2)	30 mV

NOTE: Other conditions may be appropriate. Refer to the instrumentation manual.

7.2 Sample introduction.

7.2.1 Carefully fill a 10-µL syringe with 2 to 5 µL of sample depending on the expected concentration of total chlorine. Inject the sample through the septum onto the cool boat, being certain to touch the boat with the needle tip to displace the last droplet.

7.2.2 For viscous samples that cannot be drawn into the syringe barrel, a positive displacement micropipet may be used. Here, the 2-5 µL of sample is placed on the boat from the micropipet through the opened hatch port. The same technique as with the syringe is used to displace the last droplet into the boat. A tuft of quartz wool in the boat can aid in completely transferring the sample from the micropipet into the boat.

NOTE: Dilution of samples to reduce viscosity is not recommended due to uncertainty about the solubility of the sample and its chlorinated constituents. If a positive displacement micropipet is not available, dilution may be attempted to enable injection of viscous samples.

7.2.3 Alternatively, the sample boat may be removed from the instrument and tared on an analytical balance. A sample of 2-5 mg is accurately weighed directly into the boat and the boat and sample returned to the inlet of the instrument.

2-5 µL = 2-5 mg

NOTE: Sample dilution may be required to ensure that the titration system is not overloaded with chlorine. This will be somewhat system dependent and should be determined before analysis is attempted. For example, the MCTS-20 can titrate up to 10,000 ng chlorine in a single injection or weighed sample, while the DX-20B has an upper limit of 50,000 ng chlorine. For 2 to 5 µL sample sizes, these correspond to nominal concentrations in the sample of 800 to 2,000 µg/g and 4,000 to 10,000 µg/g, respectively. If the system is overloaded, especially with inorganic chloride, residual chloride may persist in the system and affect results of subsequent samples. In general, the analyst should ensure that the baseline returns to normal before running the next sample. To speed baseline recovery, the electrolyte can be drained from the cell and replaced with fresh electrolyte.

NOTE: To determine total chlorine, do not extract the sample either with reagent water II or with an organic solvent such as toluene or isooctane. This may lower the inorganic chlorine content as well as result in losses of volatile solvents.

7.2.4 Follow the manufacturer's recommended procedure for moving the sample and boat into the. combustion tube.

7.3 Calibration and standardization.

7.3.1 System recovery - The fraction of chlorine in a standard that is titrated should be verified every 4 hours by analyzing the standard solution (Sec. 5.7). System recovery is typically 85 percent or better. The pyrolysis tube should be replaced whenever system recovery drops below 75 percent.

NOTE: The 1,000 µg/g system recovery sample is suitable for all systems except the MCTS-20 for which a 100 µg/g sample should be used.

7.3.2 Repeat the measurement of this standard at least three times.

7.3.3 System blank - The blank should be checked daily with isooctane. It is typically less than 1 µg/g chlorine. The system blank should be subtracted from both samples and standards.

7.4 Calculations.

7.4.1 For systems that read directly in mass units of chloride, the following equations apply:

$$\text{Chlorine, µg/g (wt/wt)} = \frac{\text{Display}_s}{(V_s)(D_s)(RF)} - B \qquad (3)$$

or

$$\text{Chlorine, pg/g (wt/wt)} = \frac{\text{Displays}}{(M)} - B \qquad (4)$$

where:

Display = Integrated value in nanograms (when the integrated values are displayed in micrograms, they must be multiplied by 10^3)

Display_B = blank measurement

Display_s = sample measurement

V = Volume of sample injected in microliters
- V_B = blank volume
- V_S = sample volume

D = Density of sample, grams per cubic centimeters
- D_B = blank density
- D_S = sample density

RIF = Recovery factor = ratio of chlorine = determined in standard minus the system blank, divided by known standard content $= \dfrac{\text{Found - Blank}}{\text{Known}}$

B = System blank, µg/g chlorine = $\dfrac{\text{Display}_B}{(V_B)\,(D_B)}$

M = Mass of sample, mg

7.4.2 Other systems internally compensate for recovery factor, volume, density, or mass and blank, and thus read out directly in parts per million chlorine units. Refer to instrumentation manual.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Each sample should be analyzed twice. If the results do not agree to within 10 percent, expressed as the relative percent difference of the results, repeat the analysis.

8.3 Analyze matrix spike and matrix spike duplicates - spike samples with a chlorinated organic at a level of total chlorine commensurate with the levels being determined. The spike recovery should be reported and should be between 80 and 120 percent of the expected value. Any sample suspected of containing greater than 25 percent water should also be spiked with organic chlorine.

9.0 METHOD PERFORMANCE

9.1 These data are based on 66 data points obtained by 10 laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. One laboratory and four additional data points were determined to be outliers and are not included in these results.

9.2 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method the following values only in 1 case in 20 (see Table 1):

Repeatability = 0.137 x*

*where x is the average of two results in µg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

Reproducibility = 0.455 x*

*where x is the average value of two results in µg/g.

9.3 Bias. The bias of this test method varies with concentration, as shown in Table 2:

Bias = Amount found - Amount expected

10.0 REFERENCE

1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels." Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA80. July 1988.

2. Rohrobough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

3. Standard Instrumentation, 3322 Pennsylvania Avenue, Charleston, WV 25302.

TABLE 1.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY MICROCOULOMETRIC TITRATION

Average value µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	69	228
1,000	137	455
1, 500	206	683
2,000	274	910
2,500	343	1,138
32000	411	1,365

TABLE 2.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY MICROCOULOMETRIC TITRATION

Amount expected, µg/g	Amount found µg/g	Bias, µg/g	Percent bias
320	312	-8	-3
480	443	-37	-8
920	841	-79	-9
1,498	1,483	-15	-1
1,527	1,446	-81	-5
3,029	3,016	-13	.0
3,045	2,916	-129	-4

METHOD 9076 TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS BY OXIDATIVE COMBUSTION AND MICROCOULOMETRY